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STATISTICAL EVALUATION OF THE RELATIONSHIP BETWEEN THE METALLIC ELEMENTS THAT MIGRATE FROM AISI304 AND AISI321 STAINLESS STEEL SAMPLES IN SIMULANT SOLUTIONS AT DIFFERENT IMMERSION TIMES

***Silviu-Gabriel STROE[1]**

[1]Stefan cel Mare University of Suceava, Faculty of Food Engineering,
13 Universitatii Street, 720229, Suceava, Romania
silvius@fia.usv.ro
*Corresponding author
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Abstract: *The aim of this paper was to evaluate the relationship between the metallic elements that migrate from AISI304 and AISI321 stainless steel samples in acidic food simulant solutions at different immersion times. In this study were used simulant solutions with different concentrations of acetic acid in double distilled water, different stiring environment and different immersion times of metal samples in corrosive solutions. To achieve this purpose, the experimental data were statistically processed by analyzing the correlation between variables based on Pearson correlation matrix and analyze relationships between variables by the Principal Component Analysis method (PCA). The influence of the immersion time on the dissolution rate of the Cr, Mn, ^{56}Fe and Ni metal ions from AISI304 stainless steel samples and the Ti, Cr, Mn, ^{56}Fe and Ni metal ions from AISI321 stainless steel samples was studied. The results obtained and the conclusions reached, demonstrates that the statistical method used in this study is a useful tool for studying the dissolution phenomena of metal ions in acidic food environments.*

Keywords: *stainless steel samples, acetic acid, principal components analysis, correlation matrix, Pearson's coefficients*

1. Introduction

In the last decade, globally, the food industry, from processing industry, continuing with supply chain and to the preparation of food, on observed a growing interest for research in the food safety field. In the European Union also notes that an integrated approach to this vast field, through monitoring and appropriate action, ensuring at the same time, an efficient operation of the market. Thus, a pole of interest, that is the subject of numerous multidisciplinary researches and which gather the food industry technology specialists, specialists in materials engineering and chemists, is the interface processes that occur during the contact of metallic materials on supply chain and food environments. During these stages of processing, the materials of the processing equipments, storage tanks, transmission lines or other materials intended to come into contact with food, are a chemical substances source of food or beverage contaminating. The aim of this paper was to assess the relationship between the metallic elements which migrate from

AISI304 and AISI321 stainless steel samples into acidic food simulant environments, at different immersion times. These studies are a continuation of those presented in a previous paper, where he studied the relationship between the migration of metal ions from metal samples at different concentrations of food simulant solutions [1].

2. Materials and Methods

2.1. Materials, experimental conditions and statistical methods

Considering the fact that the most aggressive environments that we encounter in industrial food raw materials processing are acidic environments, were chosen the AISI304 and AISI321 stainless steel grades [2], [3], [4].

In the experimental research, as corrosive solutions, the 3%, 6% and 9% acetic acid solutions were used. The acetic acid is recommended to test the migration of metal ions of the alloys that come into contact with the acidic food environmets [5]. The corrosive environments temperature which was studied the migration behavior of the metallic samples were 22, 28 and 34ºC. The corrosive environments stirring was 0, 125 and 250 rpm. The exposure times of the metal samples were 30, 60 and 90 min.

To analyze the chemical composition of corrosive environments, before and after their use in corrosion tests, the mass spectrometry with inductively coupled plasma (*ICP-MS*) was chosen and used, considering the advantages it presents this method over other methods. The experimental data were statistically processed by correlation analysis of the variables based on *Pearson correlation matrix* and analyze relationships between variables by *Principal Component Analysis (PCA)*. The evaluation of relationships between metal elements was performed using the trial version of SPSS v16.0 software.

The Pearson correlation matrix is a square matrix symmetrical with respect to the main diagonal that highlights the values of the coefficients of correlation (r) of the variable, taking into account two by two. The correlation coefficient expresses the intensity of association between variables and is determined with Equation 1.

$$r_{x,y} = \frac{s_{x,y}}{s_x \cdot s_y} \quad (1)$$

where,

s_x and s_y are the standard deviations

$s_{x,y}$ is the covariance between x and y values calculated using:

$$s_{x,y} = \frac{1}{n-1} \sum_{i=1}^{n} (x_i - m_x)(y_i - m_y) \quad (2)$$

where,

n=1…27 (experience number);

x_i and y_i are the variable values of x and y;

m_x and m_y are the arithmetic averages strings of the values of the two variables.

When the size of the correlation coefficient is closer to the value *±1*, is stronger association between variables, and it is closer to 0, the combination is lower. Link direction is given by the sign of the correlation coefficient.

A positive value of the *Pearson correlation coefficient* indicates a direct relationship between the two variables in the sense that to an increase of the value of a variable corresponds to an increase of the value of the other variable. A negative value of the Pearson correlation coefficient indicates an inverse relationship between the two variables in the sense that to an increase in value of the variable corresponds to a decrease in the value of other variables. To take into account the correlation it has to correspond to a

P<0.05 significance level, a level that was chosen at start of statistics study.

By applying the technique of the multivariate analysis there is a reduction of the number of variables to a relatively small number of components uncorrelated with each other, called *principal components*, by maintaining as much as possible the variance of the original data.

Only major components that have eigenvalues greater than 1 were chosen [6], because they provide more information than the original variables.

These eigenvalues measure the amount of variance explained by each principal component.

The numbers of principal components have to explain over 70% of the total variance of the data [7].

The experimental data were processed by analyzing the correlation between variables based on Pearson correlation matrix and analyze relationships among variables by the Principal Component Analysis method (PCA), using SPSS software v16.0.

3. Results and Discussion

The minimum and maximum value, mean and standard deviation for each of the metal ions of chromium, manganese, iron and nickel migrated from AISI304 stainless steel samples into simulant solutions after 30, 60 and 90 min. are shown in Table 1.

Table 1.

Specific values of metal ions which released from the AISI304 stainless steel samples in the simulant solutions after 30, 60 and 90 min.

Metal ions released in solutions	* Notations used for the metal ion released after 30, 60 and 90 min.	Calculated value. [*ppb*]			
		Minimum value, x_{min}	Maximum value, x_{max}	Average value, $\overline{X}$	Standard deviation, SD
Chromium	Cr_30	1.00	77.00	10.77	14.54
	Cr_60	1.00	188.00	17.62	34.69
	Cr_90	3.00	238.00	29.66	47.88
Manganese	Mn_30	0.72	22.00	2.99	3.92
	Mn_60	0.92	41.00	4.73	7.75
	Mn_90	0.82	43.00	7.52	9.09
Iron	Fe_30	10.00	2850.00	307.03	533.30
	Fe_60	30.00	4450.00	398.51	827.23
	Fe_90	10.00	3750.00	642.59	823.14
Nickel	Ni_30	3.30	561.00	158.29	212.59
	Ni_60	3.80	381.00	116.42	144.34
	Ni_90	5.20	361.00	98.18	114.21

* Cr_30, Mn_30, Fe_30, Ni_30 – metal ions of chromium, manganese, iron and nickel that release into simulant solution after 30 min.; Cr_60, Mn_60, Fe_60, Ni_60 – metal ions of chromium, manganese, iron and nickel that release into simulant solution after 60 min.; Cr_90, Mn_90, Fe_90, Ni_90 – metal ions of chromium, manganese, iron and nickel that release into simulant solution after 90 min.

The minimum and maximum value, mean and standard deviation for each of the metal ions of titanium, chromium, manganese, iron and nickel from AISI321 stainless steel samples into simulant solutions after 30, 60 and 90 min. are shown in the Table 2.

Table 2.

Specific values of metal ions which released from the AISI321 stainless steel samples in the simulant solutions after 30, 60 and 90 min.

Metal ions released in solutions	* Notations used for the metal ion released after 30, 60 and 90 min.	Calculated value. [*ppb*]			
		Minimum value, x_{min}	Maximum value, x_{max}	Average value, $\overline{X}$	Standard deviation, SD
Titanium	Ti_30	0.40	2.20	1.03	0.48
	Ti_60	0.70	4.98	1.77	0.96
	Ti_90	0.88	8.28	2.43	1.52
Chromium	Cr_30	1.00	21.00	7.25	5.14
	Cr_60	1.00	24.00	10.51	5.27
	Cr_90	4.00	49.00	18.66	11.06
Manganese	Mn_30	2.49	5.77	4.34	1.03
	Mn_60	2.99	11.57	5.99	2.06
	Mn_90	3.29	19.73	8.91	3.49
Iron	Fe_30	110.00	770.00	350.74	172.73
	Fe_60	150.00	1070.00	455.18	205.50
	Fe_90	160.00	1370.00	564.44	245.64
Nickel	Ni_30	7.70	696.00	169.40	229.43
	Ni_60	10.70	746.00	196.59	256.96
	Ni_90	14.70	806.00	230.11	289.50

[*] Ti_30, Cr_30, Mn_30, Fe_30, Ni_30 – metal ions of titanium, chromium, manganese, iron and nickel that release into simulant solution after 30 min.; Ti_60, Cr_60, Mn_60, Fe_60, Ni_60 – metal ions of titanium, chromium, manganese, iron and nickel that release into simulant solution after 60 min.; Ti_90, Cr_90, Mn_90, Fe_90, Ni_90 – metal ions of titanium, chromium, manganese, iron and nickel that release into simulant solution after 90 min.

After the immersion time of 30, 60 and 90 minutes in the simulate solutions the correlation coefficient values (Table 3) indicate strong correlation ($r > 0,700$), significant at $p = 0.01$, between the chromium, manganese and iron ions that migrate in corrosive solutions for AISI304. Strong correlations between the iron and manganese ions for AISI304 on the same immersion time of 30, 60 and 90 minutes were obtained.

Table 3.

Pearson correlation matrix of ions released from AISI304 stainless steel samples into simulant solutions after 30, 60 şi 90 min.

	Cr_30	Cr_60	Cr_90	Mn_30	Mn_60	Mn_90	Fe_30	Fe_60	Fe_90	Ni_30	Ni_60	Ni_90
Cr_30	1.000											
Cr_60	0.961[a]	1.000										
Cr_90	0.914[a]	0.905[a]	1.000									
Mn_30	**0.926[a]**	0.971[a]	0.905[a]	1.000								
Mn_60	0.882[a]	**0.940[a]**	0.859[a]	0.936[a]	1.000							
Mn_90	0.872[a]	0.836[a]	**0.963[a]**	0.845[a]	0.778[a]	1.000						
Fe_30	**0.948[a]**	0.970[a]	0.899[a]	**0.980[a]**	0.929[a]	0.848[a]	1.000					
Fe_60	0.935[a]	**0.981[a]**	0.916[a]	0.988[a]	**0.938[a]**	0.837[a]	0.976[a]	1.000				
Fe_90	0.537[a]	0.496[a]	**0.791[a]**	0.544[a]	0.498[a]	**0.817[a]**	0.523[a]	0.546[a]	1.000			
Ni_30	0.255	0.060	0.009	-0.061	0.025	0.037	0.023	-0.051	-0.159	1.000		
Ni_60	0.309	0.157	0.085	0.043	0.160	0.075	0.103	0.059	-0.102	0.953[a]	1.000	
Ni_90	0.453[b]	0.359	0.311	0.270	0.425[b]	0.257	0.329	0.301	0.143	0.754[a]	0.879[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

After the immersion time of 30, 60 and 90 minutes in the simulate solutions the correlation coefficient values (Table 4) indicate strong correlation (*r > 0,700*), significant at *p = 0.01*, between the titanium, chromium, manganese and iron ions that migrate in corrosive solutions for AISI321. Strong correlations between the iron and manganese ions for AISI321 stainless steel samples on the immersion time of 90 minutes were obtained.

Table 4.

Pearson correlation matrix of ions released from AISI321 stainless steel samples into simulant solutions after 30, 60 şi 90 min.

	Ti_30	Ti_60	Ti_90	Cr_30	Cr_60	Cr_90	Mn_30	Mn_60	Mn_90	Fe_30	Fe_60	Fe_90	Ni_30	Ni_60	Ni_90
Ti_30	1.000														
Ti_60	0.795[a]	1.000													
Ti_90	0.561[a]	0.919[a]	1.000												
Cr_30	0.323	0.253	0.168	1.000											
Cr_60	0.465[b]	0.282	0.105	0.647[a]	1.000										
Cr_90	0.207	0.004	-0.079	0.511[a]	0.769[a]	1.000									
Mn_30	0.294	0.331	0.296	**0.408[b]**	0.268	0.013	1.000								
Mn_60	0.530[a]	**0.607[a]**	0.557[a]	0.354	0.199	-0.033	0.772[a]	1.000							
Mn_90	0.761[a]	0.825[a]	**0.704[a]**	0.518[a]	0.392[b]	0.148	0.549[a]	0.795[a]	1.000						
Fe_30	0.345	0.133	0.072	**0.568[a]**	0.356	0.552[a]	0.369	0.483[b]	0.487[b]	1.000					
Fe_60	0.484[b]	0.258	0.110	0.673[a]	**0.460[b]**	0.499[a]	0.463[b]	**0.580[a]**	0.631[a]	0.931[a]	1.000				
Fe_90	0.517[a]	0.398[b]	0.282	0.633[a]	0.461[b]	**0.429[b]**	0.536[a]	0.680[a]	**0.721[a]**	0.841[a]	0.940[a]	1.000			
Ni_30	0.230	0.516[a]	0.613[a]	-0.179	0.034	-0.157	-0.107	0.168	0.232	-0.372	-0.335	-0.152	1.000		
Ni_60	0.240	**0.495[a]**	0.594[a]	-0.175	0.036	-0.158	-0.102	0.150	0.213	-0.368	-0.337	-0.157	0.994[a]	1.000	
Ni_90	0.233	0.470[b]	**0.557[a]**	-0.189	0.044	-0.149	-0.105	0.153	0.204	-0.367	-0.331	-0.160	0.993[a]	0.995[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

Principal components analysis reveals that the first two principal components explain 95.08% of total variance (*PC1 = 74.16%* and *PC2 = 20.92%*) (Figure 1).

Regarding the first principal component (*PC1*), it can be seen that there is very good correlation between the ions of iron, chromium and manganese released from the AISI304 stainless steel samples in the simulant solutions after 30 and 60 min.. These variables are strongly associated with first principal component (*PC1*). Also, from the first principal component (*PC1*) is remarkable direct correlation between the manganese ions and chromium which migrate after 90 min. of exposure (*Mn_90* and *Cr_90*). The second principal component (*PC2*) highlights the difference between the iron and nickel ions that released into simulant solutions after 90 min. (*Fe_90* and *Ni_90*).

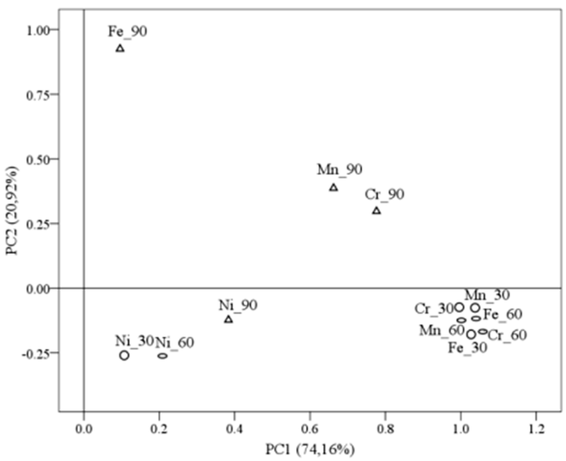

Figure 1. Relationships between the chromium, manganese, iron and nickel metal ions released from AISI304 stainless steel samples into 3, 6 and 9% CH_3COOH solutions at 30, 60 and 90 min. immersion times.

The correlation matrix of the metal ions that migrate from AISI321 stainless steel samples into simulant solution after an 30, 60 and 90 min. immersion time (Table 4) shows no statistically significant correlation between them. A significant association ($r = 0.607$, at a $p = 0.01$ level) resulted between the titanium and manganese ions that migrate into the simulated acetic acid solution after 60 min. Increasing the immersion time of 90 min. determines a strong association ($r = 0.704$, at a $p = 0.01$ level) among the titanium and manganese ions.

A significant association ($r = 0.568$, at a $p = 0.01$ level) was obtained between chromium and iron ions released from AISI321 stainless steel samples into the simulated solution an 30 min. immersion time.

Also, between the chromium and iron ions are moderate association significant at 60 min. immersion time ($r = 0.469$ at a $p = 0.05$ level), and at 90 min. immersion time ($r = 0.429$).

Significant correlations at $p = 0.01$ level between manganese and iron ions migrated from stainless steel samples into the simulant solution after 60 min. immersion time ($r = 0.580$) and after the 90 min. immersion time ($r = 0.721$) were obtained.

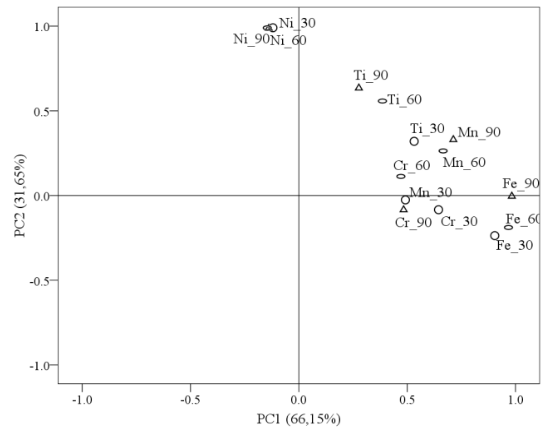

Figure 2. Relationships between the titanium, chromium, manganese, iron and nickel metal ions released from AISI321 stainless steel samples into 3, 6 and 9% CH_3COOH solutions at 30, 60 and 90 min. immersion times.

It can be said that immersing of the AISI321 stainless steel samples into a simulated solution for 30 min. highlights significant correlation between chromium and iron ions, and that correlations have been obtained between titanium and manganese, chromium and iron, manganese and iron ions that have released from the AISI321 stainless steel samples into simulant solution after 30 min and 90 min. The first two principal components (*PC1*) and (*PC2*) (Figure 2), explained 97.80% of data variance, with PC1 explaining 66.15%. From the graphical representation of the relationships between metal ions that release from AISI321 stainless steel samples into the simulant solutions on observed along PC1 axis close relationship between titanium, chromium, manganese and iron ions after 30, 60 and 90 min. immersion time. The variables position relative to the first principal component show that there exists a strong direct relationship. Since the variables are the same quadrant, the relationship between them is positive. *PC2* indicates the association between nickel ions that release into simulated solution at 30, 60 and 90 min. immersion times, and Ni_30 variables, Ni_60 and Ni_90 that are strongly associated with the major component. Towards the second principal component (*PC2*) is shown in the graphic representation the opposition between the iron and nickel ions that released from AISI321 stainless steel samples into simulated solution to a 30, 60 and 90 min immersion time, with negative correlation.

4. Conclusion

Regarding the influence of the immersion time of the metallic samples into acidic simulant solutions, was observed that at 30 min. immersion time, as well an 60 min. immersion time of the AISI304 stainless steel samples occurs a migration phenomenon of the iron, chromium and manganese ions, as compared with nickel ions that migrate after the same immersion time. For all immersion times studied, the iron ions that migrate from AISI321 stainless steel samples into the simulant, compared to the behavior in the same conditions of the nickel ions. The iron ions migrate from AISI321 stainless steel samples into the simulated solution at all three times of immersion forms a distinct group of nickel ions migrate at the same operating parameters. It can be concluded that the extreme positions on the diagram of the principal components of the two groups shows that, from the point of view of the studied variables, between the two groups the greatest differences were obtained.

5. References

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