STUDY ON RELATIONSHIPS BETWEEN METAL IONS MIGRATED FROM FOOD STAINLESS STEEL GRADES INTO FOOD SIMULANT SOLUTIONS AT VARIOUS IMMERSION TEMPERATURES

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Abstract: The aim of this study was to study the relationship between metallic elements migrated from AISI304 and AISI321stainless steel grades into simulant solutions (3%, 6% and 9% acetic acid in double-distilled water) at 22, 28 and 34°C by statistical methods. The migration of Cr, Mn, Fe and Ni ions from AISI304 stainless steel grade, Ti, Cr, Mn, Fe and Ni from AISI321stainless steel grade respectively was studied. The correlation between variables - ions which migrate from stainless steel samples - based on Pearson correlation matrix was analyzed to fulfill its purpose and Principal Component Analysis (PCA) statistical method was used to explain the similarities or differences between them.The results indicate on one hand a strong corelation between Cr, Fe and Mn ions migrated from AISI304 stainless steel samples and on the other hand a strong one between Mn and Fe ions migrated from AISI321 stainless steel samples into simulant solutions.

Key word: migration, simulant solution, immersion temperatures, Pearson correlation matrix, principal component analysis.

Introduction

In the last decade, globally, beginning with the processing industry and continuing with the supply chain, food industry has shown a growing interest for advanced research in the field of food safety. During these processing steps, the equipment materials, storage tanks, pipelines or other materials intended to come into contact with foodstuffs, interact with food environments. This is a source of chemical contaminants that may endanger the consumers' health (Ba,07), (Re,02), (Po,07), (Po,09).

Chemical migration of constituents from equipment materials into food must not occur in amounts that endanger consumers' health. Thus, at international level a set of regulations regarding materials intended to come into contact with food environments (EU,04) was established. It is known that the metallic alloys used for the construction of processing equipment are stainless steel. Thus, most studies have focused on the study of the behavior of stainless steels in food environments (Br,12), (He,08), (St,11).

The aim of this study was to study the relationships between metallic elements migrated from AISI304 and AISI321 stainless steel samples into simulant solutions at various immersion temperatures by statistical methods.

Therefore, the Principal Component Analysis method was used in order to study the relationships between metal ions migrating from stainless steel samples into acidic simulant solutions. This method was also used by other authors to study the phenomena of migration into food environments (Bo,12), (Ro,02).

Materials and methods

AISI304 and AISI321 stainless steel samples were used in order to study the relationship between metal ions migrating into simulant solutions. Working parameters used in migration tests were the following: 3%, 6% and 9% acetic acid in double-distilled water were used as corrosive simulant solutions, simulants recommended by the European regulation (Gr,08), immersion temperatures: 22, 28 and 34°C, stirring environment - 0, 125 and 250 rot/min and the exposure times: 30, 60 and 90 min. After carrying out the migration tests, the concentrations of metal ions in simulant solution were analyzed by ICP-MS method, being used in statistical analysis. The relationships between metal ions were studied by Pearson's correlation matrix with statistical significance at $p<0.05$ and Principal Component Analysis (PCA) method. Pearson correlation matrix is a symmetric square matrix by main diagonal that emphasizes values of correlation coefficients (r) between variables, the correlation coefficient value showing the intensity of association between variables. The size of the correlation coefficient is between ± 1.

The PCA method is a multivariate analysis technique that can be applied to original data to reduce the number of variables by converting the variables under investigation into new variables, namely principal components (PCs) minimizing the correlation among the original variables (St,13).

Principal components (PC) were extracted as a linear combination of original variables. The first principal component extracted (PC1) is the linear combination of variables that take the most of the variance of the original data and the second principal component (PC2) takes a smaller variance compared to the first component (PC1). Only the principal components having eigenvalues higher than 1 were chosen, because they provide more information than the original variables.The graphical representation allows the viewing of the relationships between variables and identification of possible groups of variables. Pearson's correlation matrix and principal component analysis were carried out using SPSS v.16.0 -trial version software.

Results and Discussion

Minimum and maximum value, average value and standard deviation for the chromium, manganese, iron and nickel ions migrating from AISI304 and AISI321stainless steel samples into acidic simulant solutions at 22ºC, 28ºC and 34ºC are shown in Table 1 and Table 2.

Pearson correlation matrices of ions migrating from AISI304and AISI321 stainless steel samples into 3%, 6% and 9% acidic simulant solutions at 22ºC, 28ºC and 34ºC are shown in Table 3 and Table 4.

Strong correlations between chromium - manganese ions at 22ºC ($r=0.967$), between chromium - iron ions at 34ºC ($r=0.946$), between chromium – manganese ions at 34ºC ($r=0.925$) and manganese - iron ions migrating from stainless steel samples into acidic simulant solutions at 34ºC ($r=0.908$) can be observed from the study of Pearson's correlation matrix for AISI304 (Table 3).

Strong correlations between: chromium - manganese ions at 22ºC ($r=0.700$), between chromium - iron ions at 22ºC ($r=0.700$), manganese - iron ions at 22ºC ($r=0.719$) ab), manganese - iron ions at 28ºC ($r=0.678$) migrating from AISI321 stainless steel samples into acidic simulant solutions can be observed as well.

Table 1. Specific values of metal ions migrating from the AISI304 stainless steel samples into acidic simulant solutions at 22, 28 and 34°C.

Metal ions migrated into solutions	*Notations used for metal ions migrated into solutions at 22, 28 and 34°C	Calculated value, [*ppb*]			
		Minimum value, x_{min}	Maximum value, x_{max}	Average value, $\overline{X}$	Standard deviation, SD
Chromium	Cr_22	1.00	238.00	24.77	56.57
	Cr_28	2.00	42.00	12.74	8.51
	Cr_34	0.72	108.00	20.06	23.66
Manganese	Mn_22	0.82	43.00	6.57	11.15
	Mn_28	0.72	12.67	3.79	2.88
	Mn_34	0.82	25.00	4.88	5.66
Iron	Fe_22	10.00	4450.00	562.96	1024.34
	Fe_28	10.00	580.00	270.00	169.09
	Fe_34	10.00	3750.00	515.18	761.31
Nickel	Ni_22	3.30	470.00	162.38	196.23
	Ni_28	5.60	551.00	117.46	171.40
	Ni_34	5.70	561.00	122.72	165.39

* Cr_22, Mn_22, Fe_22, Ni_22 – metal ions of chromium, manganese, iron and nickel migrating at 22°C;
Cr_28, Mn_28, Fe_28, Ni_28 – metal ions of chromium, manganese, iron and nickel migrating at 28°C;
Cr_34, Mn_34, Fe_34, Ni_34 – metal ions of chromium, manganese, iron and nickel migrating at 34°C.

Table 2. Specific values of metal ions migrating from the AISI321 stainless steel samples into acidic simulant solutions at 22, 28 and 34°C.

Metal ions migrated into solutions	*Notations used for metal ions migrated into solutions at 22, 28 and 34°C	Calculated value, [*ppb*]			
		Minimum value, x_{min}	Maximum value, x_{max}	Average value, $\overline{X}$	Minimum value, x_{min}
Titanium	Ti_22	0.40	3.08	1.30	0.76
	Ti_28	0.50	3.20	1.44	0.66
	Ti_34	.98	8.28	2.50	1.61
Chromium	Cr_22	1.00	21.00	7.59	4.60
	Cr_28	1.00	37.00	13.40	8.61
	Cr_34	1.00	49.00	15.44	10.88
Manganese	Mn_22	2.69	8.49	5.01	1.45
	Mn_28	3.63	10.57	6.71	2.09
	Mn_34	2.49	19.73	7.52	4.32
Iron	Fe_22	110.00	670.00	288.88	131.09
	Fe_28	160.00	870.00	505.18	175.74
	Fe_34	290.00	1370.00	576.29	248.02
Nickel	Ni_22	7.70	456.00	138.55	171.27
	Ni_28	13.70	756.00	205.48	269.11
	Ni_34	17.70	806.00	252.07	309.65

* Ti_22, Cr_22, Mn_22, Fe_22, Ni_22 – metal ions of titanium, chromium, manganese, iron and nickel migrating at 22°C;
Ti_28, Cr_28, Mn_28, Fe_28, Ni_28 – metal ions of titanium, chromium, manganese, iron and nickel migrating at 28°C;
Ti_34, Cr_34, Mn_34, Fe_34, Ni_34 – metal ions of titanium, chromium, manganese, iron and nickel migrating at 34°C;

Table 3. Pearson correlation matrix of ions migrated from AISI304 stainless steel grade into acidic simulant solutions at 22, 28 and 34°C.

	Cr_22	Cr_28	Cr_34	Mn_22	Mn_28	Mn_34	Fe_22	Fe_28	Fe_34	Ni_22	Ni_28	Ni_34
Cr_22	1.000											
Cr_28	-0.004	1.000										
Cr_34	0.614[a]	0.308	1.000									
Mn_22	**0.967[a]**	-0.055	0.536[a]	1.000								
Mn_28	0.301	**0.817[a]**	0.534[a]	0.233	1.000							
Mn_34	0.620[a]	0.352	**0.925[a]**	0.537[a]	0.618[a]	1.000						
Fe_22	**0.873[a]**	-0.037	0.341	**0.903[a]**	0.248	0.377	1.000					
Fe_28	0.220	**0.486[b]**	0.518[a]	0.161	**0.713[a]**	0.565[a]	0.169	1.000				
Fe_34	0.706[a]	0.105	**0.946[a]**	0.621[a]	0.389[b]	**0.908[a]**	0.399[b]	0.462[b]	1.000			
Ni_22	0.103	0.726[a]	0.160	0.092	0.382[b]	0.070	0.042	0.043	0.028	1.000		
Ni_28	-0.113	0.441[b]	-0.034	-0.095	0.000	-0.157	-0.134	-0.157	-0.106	0.854[a]	1.000	
Ni_34	-0.050	0.534[a]	0.081	-0.063	0.133	-0.034	-0.101	-0.068	-0.002	0.888[a]	0.979[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 4. Pearson correlation matrix of ions migrated from AISI321 stainless steel grade into acidic simulant solutions at 22, 28 and 34°C.

	Ti_22	Ti_28	Ti_34	Cr_22	Cr_28	Cr_34	Mn_22	Mn_28	Mn_34	Fe_22	Fe_28	Fe_34	Ni_22	Ni_28	Ni_34
Ti_22	1.000														
Ti_28	0.731[a]	1.000													
Ti_34	0.683[a]	0.626[a]	1.000												
Cr_22	0.313	0.429[b]	0.283	1.000											
Cr_28	0.195	0.463[b]	0.199	0.621[a]	1.000										
Cr_34	0.121	0.338	0.062	0.778[a]	0.702[a]	1.000									
Mn_22	**0.406[b]**	0.639[a]	0.397[b]	**0.700[a]**	0.576[a]	0.758[a]	1.000								
Mn_28	0.616[a]	**0.809[a]**	0.399[b]	0.579[a]	**0.539[a]**	0.448[b]	0.704[a]	1.000							
Mn_34	0.654[a]	0.805[a]	**0.777[a]**	0.465[b]	0.430[b]	0.275	0.608[a]	0.766[a]	1.000						
Fe_22	0.228	0.506[a]	0.209	**0.700[a]**	0.439[b]	0.555[a]	**0.719[a]**	0.650[a]	0.581[a]	1.000					
Fe_28	0.127	0.563[a]	0.125	0.538[a]	**0.436[b]**	0.421[b]	0.646[a]	**0.678[a]**	0.499[a]	0.795[a]	1.000				
Fe_34	0.176	0.551[a]	0.242	0.605[a]	0.396[b]	**0.404[b]**	0.617[a]	0.694[a]	**0.610[a]**	0.905[a]	0.812[a]	1.000			
Ni_22	**0.502[a]**	0.050	0.559[a]	-0.073	-0.217	-0.117	-0.071	-0.125	0.248	-0.273	-0.599[a]	-0.319	1.000		
Ni_28	0.514[a]	0.105	0.654[a]	-0.007	-0.143	-0.088	-0.069	-0.109	0.309	-0.218	**-0.531[a]**	-0.250	0.965[a]	1.000	
Ni_34	0.519[a]	0.062	**0.575[a]**	-0.053	-0.202	-0.107	-0.072	-0.118	0.250	-0.254	-0.580[a]	-0.305	0.995[a]	0.978[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

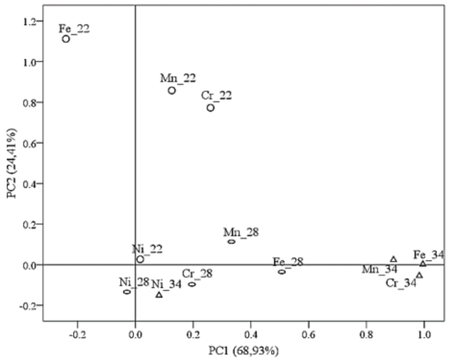

Fig. 1. PCA loading plot for metal ions migrated from AISI304 stainless steel samples into acidic solutions of concentration 3%,6% and 9% at 22, 28 and 34°C. The symbols used: ○ - ions migrated into acidic solutions at 22°C; ⬭ - ions migrated into acidic solutions at 28°C; Δ - ions migrated into acidic solutions at 34°C;

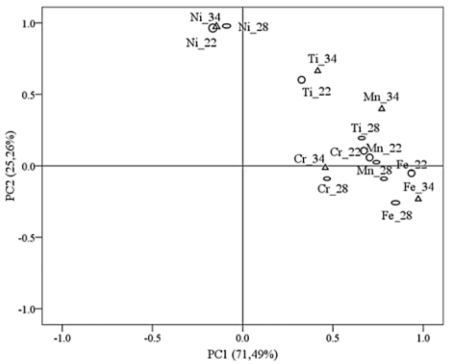

Fig. 2. PCA loading plot for metal ions migrated from AISI321 stainless steel samples into acidic solutions of concentration 3%, 6% and 9% at 22, 28 and 34°C. The symbols used: ○ - ions migrated into acidic solutions at 22°C; ⬭ - ions migrated into acidic solutions at 28°C; Δ - ions migrated into acidic solutions at 34°C;

Principal Component Analysis of the variables – ions' migration from AISI304 stainless steel grade samples into solutions at 22°C, 28°C and 34°C - highlights that the first two principal components (PC1 and PC2) explained 93,34% of the total variance of the data, the first principal component (PC1) explained 68.93% of variance and the second principal component (PC2) explained 24.41% of variance (Figure 1). Along the first principal component (PC1), a close association between the chromium, iron and manganese ions migrating from AISI304 stainless steel samples into simulant solution at 34°C can be observed, emphasizing the relationships between variables reflected by very high significant correlation coefficients (Table 3).

The second principal component (PC2) is strongly correlated with iron, manganese and chromium ions migrating from AISI304 stainless steel samples into simulant solutions at 22°C. The opposition between nickel and iron ions migrating from AISI304 stainless steel samples at 28°C can be seen in Figure 1.

Principal Component Analysis of the variables – ions' migration from AISI321 stainless steel grade samples into solutions at 22°C, 28°C and 34°C - highlights that the first two principal components (PC1 and PC2) explained 96.75% of the total variance of the data, first principal component (PC1) explained 71.49% of variance and the second principal component (PC2) explained 25.26% of variance (Figure 2).Along the first principal component (PC1) a close association between the iron, manganese and chromium ions migrating from AISI321 stainless steel samples into simulant solutions at 22, 28 and 34°C can be observed.

The second principal component (PC2) is strongly correlated with nickel ions migrating from AISI321 stainless steel samples into simulant solutions at 22, 28 and 34°C. The opposition between nickel and iron ions migrating from AISI321 stainless steel samples at 22, 28 and 34°C can be observed.

Conclusions

Pearson correlation matrix and Principal Component Analysis methods were used to establish the relationships between the variables studied. The results showed significant differences regarding the relationships between nickel, manganese and chromium ions into acidic simulant solutions at various immersion temperatures. The iron, chromium and manganese ions migrate from AISI304 stainless steel samples migrated into simulant solutions especially at 34°C as against nickel ions. The iron, manganese and chromium ions migrated especially at 22°C. Strong correlations ($r = 0.967$, $p = 0.01$) between manganese and iron ions migrated from AISI304 at 22°C as well as strong correlations ($r = 0.809$, $p = 0.01$) between titanium and manganese from AISI321, migrated at 28°C can be observed. In conclusion, it can be stated that the statistical methods used in this research are powerful tools to study the relationships between various working parameters.

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