INVESTIGAREA AMBALAJELOR DE STICLĂ PRIVIND ELIBERAREA DE IONI CU POTENȚIAL DE DEGRADARE A ALIMENTELOR
INVESTIGATION OF THE GLASS CONTAINERS REGARDING THE MIGRATION OF IONS WITH FOOD DEGRADATION POTENTIAL

MIHAI EFTIMIE[1], ANA FILIP[2] * , CRISTINA TODAȘCĂ[1], LAURA ȘERBAN[1]
[1] *University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Ghe. Polizu 1-7 str., Bucharest, Romania, 011061*
[2] *National Institute for Laser, Plasma and Radiation Physics, 409 Atomiștilor str., Magurele, Ilfov, Romania, 077125*

Iron ions can change the properties of bottled foods and beverages in terms of taste, flavour, smell and colour. The paper deals with the chemical stability and the releases of Fe^{3+}, Na^+, Mg^{2+} and Ca^{2+} ions from commercial glass containers as well as from our own recipes, similar to the industrial ones. Even if, regarding the considered ions, the released amounts cannot lead to food toxicity, the Fe^{3+} migration from the elaborated glass recipes is in the range where a release – resorption mechanism could be used in the wine stabilization stage, thus making the process of wine production more efficient.

Ionii de fier pot modifica proprietățile alimentelor și băuturilor îmbuteliate în ceea ce privește gustul, aroma, mirosul și culoarea. Lucrarea urmărește stabilitatea chimică și eliberările de Fe^{3+}, Na^+, Mg^{2+} și Ca^{2+} din ambalaje de sticlă comerciale precum și din rețete proprii elaborate, similare celor industriale. Chiar dacă, în privința ionilor urmăriți, cantitățile eliberate nu pot conduce la toxicitate asupra alimentelor, migrarea Fe^{3+} din rețetele elaborate de sticlă se situează în domeniul în care un mecanism de eliberare-resorbție ar putea fi folosit în etapa de stabilizare a vinului, eficientizând procesul de obținere a vinurilor.

1. Introduction

There is no absolute and explicit method that can quantify chemical instability of glasses, they are sometimes defined by comparison with other samples. Interferometry and mass loss performed on samples attacked by aqueous solutions, as well as titration of alkalis, measurement of pH and conductivity of extracts, are methods of analysis that provide information on the stability of glasses[1]**.**

On the other hand, metals affect the organoleptic characteristics of the wine: aroma, taste, flavour, colour and freshness, mainly due to the precipitates resulted, yeasts and sediments or turbidity resulting from fermentation, maturation and storage of the wine. However, high levels of these metals produce some more effects. Some of these are defined by: pH change due to precipitation of Ca^{2+} and K^+ tartrates, oxidation of Cu^{2+} and Fe^{2+} resulting in the "oxidation" of the wine, change of freshness and aroma, appearance of precipitated tannins and the appearance of sulphur products, such as H_2S, methanethiol (MeSH) and Dimethyl sulfate (DMS), as well. The mechanism of action is complex, and studies are still being conducted on its exact evolution. According to some researchers [2-4] the mechanism of action is presented as follows: Cu^{2+}, Fe^{2+} and Mn^{2+} activate the molecular oxygen and forego the oxidation reactions of the organic compounds to aldehydes and ketones by forming reactive oxygen species. Fe^{2+} catalyses the oxidation of polyphenolic compounds that react with the acetaldehydes formed in the presence of Mn^{2+} leading to decreased stability and poor quality of wine.

Equally, ions of copper, iron and manganese have the property of reacting with aminoacids, polyphenols and melanoid compounds during maturation and storage of the product, thus causing loss of freshness and its oxidative browning. When concentrations of Cu^{2+} or Fe^{2+} exceed 1 μg/ml up to 7 μg/ml, unpleasant odours occur, leading to a decreased quality and loss of taste [2].

In 2006, Esparza et al. conducted an experiment on wines during their fermentation in the vinification process, studying the effect of the iron ions on the colour of the wine, at the specific wavelength of the red colour. Following the study, the conclusion was that iron ions produce in wine an increase in the "blue tint" and a decrease in the

---

* Autor corespondent/*Corresponding author*,
E-mail: violeta.filip3@gmail.com

"red tint", having no visible influence on the intensity of the "yellow tint"[3]. These demonstrations are consistent with the fact that anthocyanin-containing o-phenyl groups can complex iron ions, inducing bathochromic displacement (toward the blue region) [4].

Another important aspect regarding the impact of Fe^{2+} in the process of reducing oxidative stress has been intensively studied. The reactive species of oxygen and nitrogen are -OH, H_2O_2, O_2^-, NO^-, $ONOO^-$, which have the effect of distorting proteins, lipids and DNA molecules. This oxidative degradation effect is considered to be involved in the production of different types of cancer, ageing and neurodegenerative diseases such as Alzheimer's and Parkinson's [5].

The oxidation process of the DNA molecule is observed directly from the $\cdot OH$ radical and indirectly from the O_2^- oxidation of the [4Fe-4S] clusters in order to form hydrogen peroxide.

In addition to the formation of hydrogen peroxide, O_2^- also contributes to the migration of Fe^{2+} from enzymes, in the form of ferritin and [4Fe-4S], containing dehydratase, by reducing Fe^{3+} and generating an unstable iron-sulphur cluster and releasing Fe^{2+}. The superoxide also reduces Fe^{3+} and Cu^{2+} in the aqueous medium, making it possible for the interaction of metal ions with hydrogen peroxide, although the rate of reduction of iron is much slower.

Other studies have evaluated the oxidative effects of bottling on vegetable oils [6] or the effects of storage temperature of food in glass containers on the shelf-life [7].

In this context, the paper compares commercial glass containers with our own glass recipes, similar to industrial ones, made by varying the concentrations of Fe^{3+} and melting times in order to investigate the ion migration in different environments simulating bottled foods.

2. Materials and methods

Five different glass samples were prepared, which the compositions were varied, by the gradual increase of the concentration of Fe_2O_3, displacing the other oxides in the composition.

Compositions of the glasses are presented in Table 1.

All the raw material mixtures were dry homogenized for 30 minutes in a mortar, then melted in alumina crucibles in a Nabertherm 3000 oven at 1400 ° C. The melting time was 150 minutes for the first 3 samples. The samples P3_0.65_150 and P4_0.65_15 have the same composition but melting times of 150 and 15 minutes, respectively, in order to investigate the influence of melting time on chemical equilibrium, estimated through the chemical stability of the obtained glass, but also to simulate the short time the glass stays in the melting area of an industrial furnace [8]. The 150-minute plateau at melting temperature was chosen to allow the glass melt to reach the structural and thermodynamic equilibrium, based on literature data [8]. Sample P5 was developed as a sum of conditions for the "worst case scenario", which would lead to the highest probability of iron ions release: 3% Fe_2O_3 and short time (15 minutes) to reach the structural equilibrium. The glasses were poured into circular and parallelepiped shapes and annealed in a Carbolite 1000 oven at 550 ° C for 15 minutes.

To evaluate the quality of annealing, the samples were subjected to linear thermal expansion test using a NETZSCH DIL 402-PC dilatometer. The chemical stability of the glasses was determined by standardized and laboratory methods. The quantitative determinations regarding ion migration (especially Fe^{3+}) by spectrophotometric methods on iron ions migration in various solutions were made using a Thermo Scientific - Evolution 3000 UV-VIS spectrometer and for mass spectrometry with inductive coupled plasma and laser ablation using a ICP-MS Agilent 8800 ICP-MS Triple Quadrupole.

3. Results and discussion

3.1. Linear thermal expansion

Considering the analysis of linear thermal expansion as a manner to highlight the correct elaboration and annealing of a glass, the thermal expansion curves of the samples obtained in the laboratory were determined and presented in Figure 1.

The values of the thermal expansion coefficients obtained fall within the usual values of commercial glass containers (usually these

Table 1

The compositions of the prepared glasses / *Compoziţiile probelor de sticlă realizate, %gr.*

Oxide	P1_0.35_150	P2_0.5_150	P3_0.65_150	P4_0.65_15	P5_3_15
SiO₂	68.192	68.017	68.017	68.017	68.4
Al₂O₃	2.881	2.874	2.874	2.874	2.89
Fe₂O₃	**0.35**	**0.5**	**0.65**	**0.65**	**3**
CaO	7.138	7.119	7.119	7.119	7.16
MgO	2.522	2.516	2.516	2.516	2.53
Na₂O	16.849	16.805	16.805	16.805	16.9
K₂O	0.668	0.666	0.666	0.666	0.67
BaO	0.927	0.925	0.925	0.925	0.93
C	0.1	0.099	0.099	0.099	0.1
Na₂SO₄	0.478	0.477	0.478	0.478	0.48

dL/Lo *10⁻³

P1_0.35_150
Temp./°C*   T. Alpha*/(1/K)
20.0, 500.0 : 9.3885E-06*

P2_0.5_150
Temp./°C*   T. Alpha*/(1/K)
20.0, 500.0 : 9.2987E-06*

P3_0.65_150
Temp./°C   T. Alpha/(1/K)
20.0, 500.0 : 9.6729E-06

P5_3_15
Temp./°C*   T. Alpha*/(1/K)
20.0, 500.0 : 9.2736E-06*

546.8 °C
553.7 °C
558.8 °C
549.0 °C

Temperature /°C

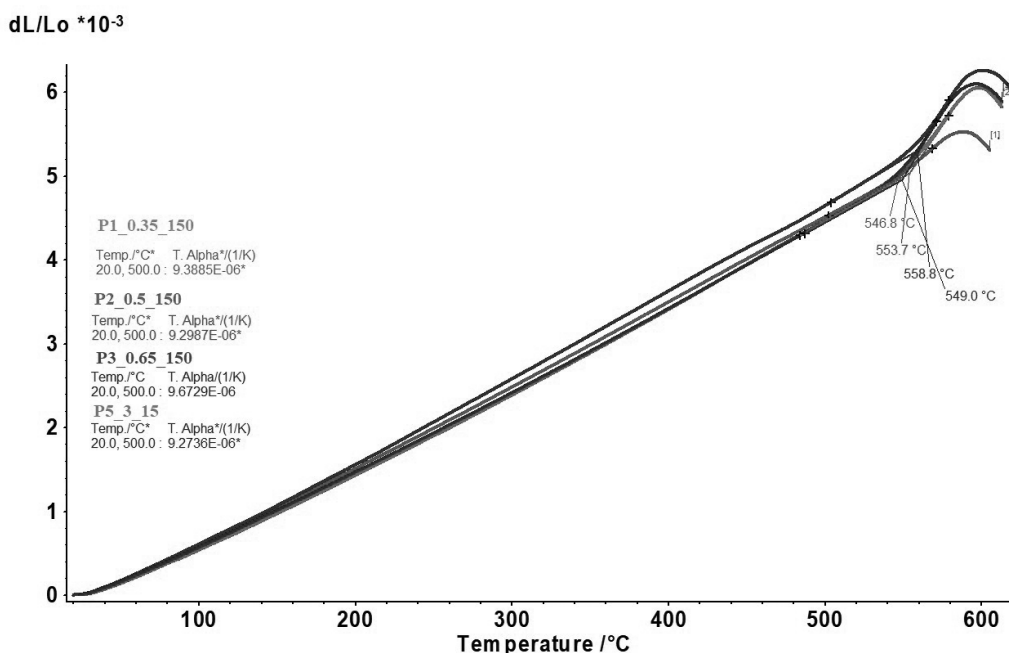Fig. 1 - Thermal expansion curves of P1_0.35_150(1), P2_0.5_150 (2), P3_0.65_150 (3) and P5_3_15 (4) samples / *Curbele de dilatare termică a probelor P1_0.35_150(1), P2_0.5_150 (2), P3_0.65_150 (3) si P5_3_15 (4).*

glasses have values between 80 and $100·10^{-7}grd^{-1}$), which means that the method of obtaining the laboratory samples is comparable with the industrial ones, thus the chemical stability tests that will be described below are relevant both in scientific and industrial context.

3.2. The hydrolytic stability measurements of the glass

Hydrolytic resistance tests were performed by two methods:
a) according to ISO 719:1985 (revised and confirmed in 2016);

b) mechanical stirring of a glass powder in water at ambient temperature of 25 ° C.

The amount of ion released is calculated as equivalent µg Na_2O/g glass, according to ISO 719:1985.

The reference sample is a borosilicate glass sample from pharmaceutical glass containers where Fe^{3+} migration is carried out in various solutions. Thus, the low value of the released ion concentration arises from the need for the highest chemical inertia of the bottle. For comparison, the same determination was made for commercial glass samples from China, Spain, Czech Republic and France. The obtained results are presented in Figure 2.
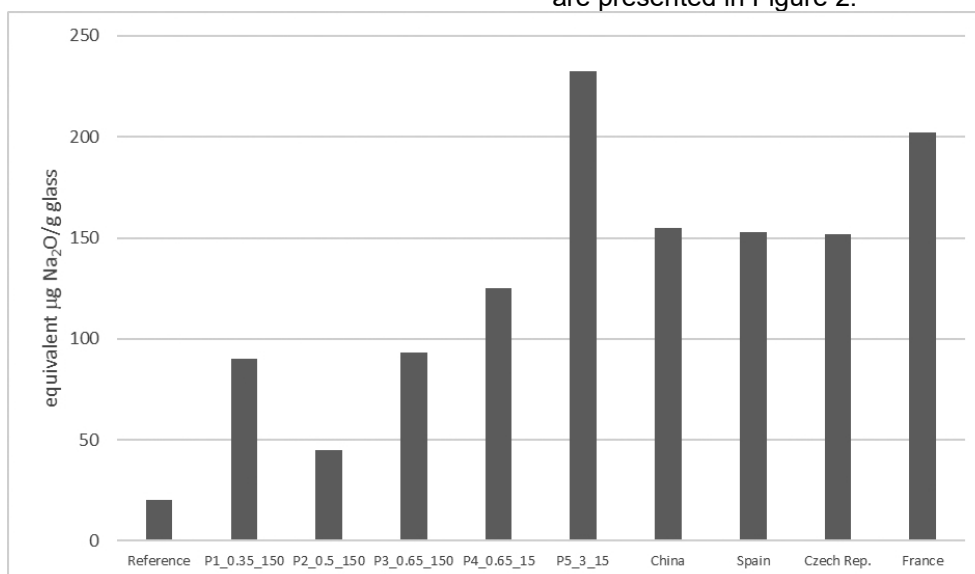
Fig. 2 - The amount of equivalent Na_2O released by the glass by heating it at 98 ºC for 60 min / *Cantitatea de echivalent Na_2O eliberată de sticlă prin încălzirea la 98 ºC timp de 60 min.*

One can see that all the samples with concentrations below 1% Fe^{3+} release smaller amounts of ions than the industrial bottles. The higher value determined for the equivalent Na_2O migrated into water for sample P5_3_15 is explained by the 3% Fe^{3+} concentration introduced.

The significant difference of the values of ion concentrations migrated from the laboratory and industrial glass samples resides in the processing method. The industrial process involves obtaining as many objects as possible in a short time to maintain economic efficiency, but the samples P1_0.35_150, P2_0.5_150 and P3_0.65_150 obtained in the laboratory were kept at the maximum melting temperature for a long period. This duration of the maximum temperature allows, first of all, a good refining of the glass, but also a structural arrangement as close as possible to the thermodynamic equilibrium, resulting in a quasi-inert material, with strong links between the component ions, which will barely release ions in the environment, even in high temperature conditions.

The used standard classifies the glasses in stability classes, from 1 to 5, where stability class 1 indicates a very stable glass. Excepting the reference sample and P2_0.5_150, all other tested glasses (presented in Table 2) are classified in the stability class 3.

As the industrial glasses had higher ion release than those produced in the laboratory, they were not subjected to any further tests.

The second method to determine the hydrolytic stability of the glass samples involves maintaining of 2 grams of grinded glass powder with a fineness below 300 µm in water at 25 °C for 3 hours under mechanical stirring and the titration of the supernatant with the 0.01 M HCl solution in the presence of methyl red. The test was performed only for the P3_0.65_150, P4_0.65_15 and P5_3_15 samples, which had the highest amounts of ions released when tested at 98 °C.

Table 2

Classification in the stability classes according to ISO 719:1985
Încadrarea în clase de stabilitate conform ISO 719:1985

Glass	Stability class
Reference sample	1
P1_0.35_150	3
P2_0.5_150	2
P3_0.65_15	3
P4_0.65_15	3
P5_3_15	3
China	3
Spain	3
Czech Republic	3
France	3

One can observe that the values of the amounts of equivalent Na_2O migrated in the second determination are lower than in the first case. The temperature appears, under these conditions, as a decisive factor of the mechanism of interaction between the glass container and the bottled aqueous environment; the increase of the temperature favours the migration of cationic species into the liquid environment.

From Figure 3, for the P3_0.65_150 sample, the amount of equivalent Na_2O migrated in solution is halved in the second determination, and for P5_3_15 sample the value decreases significantly, from 232.5 to 186 µg Na_2O.

For the samples developed in the laboratory, the influence of the processing time becomes decisive. Thus, the P4_0.65_15 sample releases an amount of more than 3 times greater of equivalent Na_2O than P3_0.65_150 sample with the same composition.

3.3. Migration of Fe^{3+} in water and citric acid

Due to the effects that iron ions have on the properties of bottled foods and beverages (changes in taste, flavour, smell, colour), the
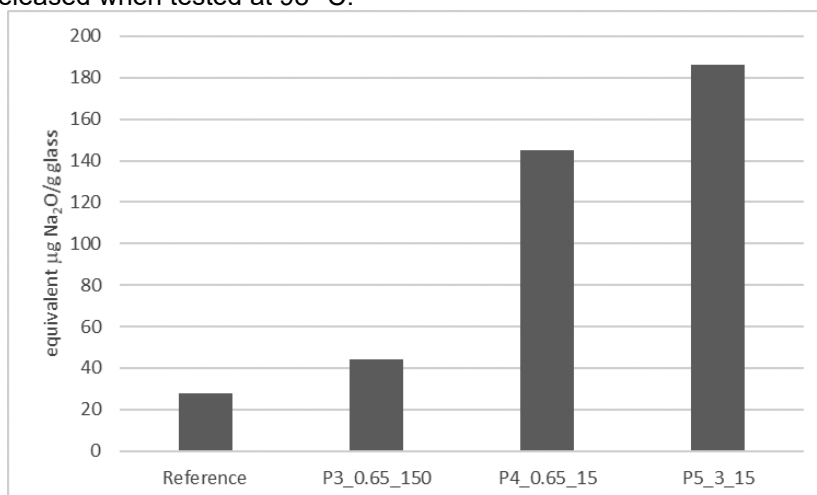

Fig. 3 - The amount of equivalent Na_2O released from the glass powder stirred at 25 °C for 3 hours / *Cantitatea de echivalent Na_2O eliberată din pulberea de sticlă ținută sub agitare la 25 ºC timp de 3 ore*
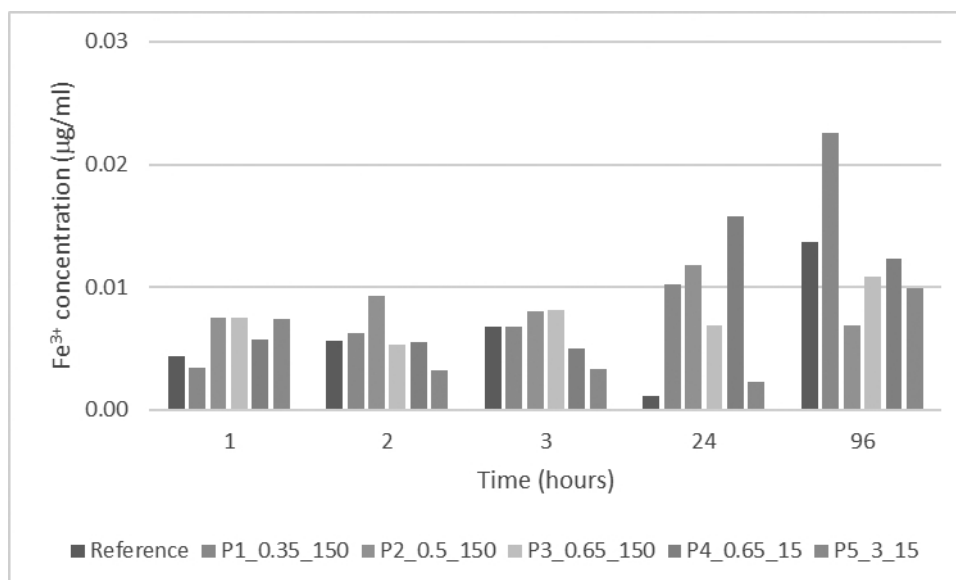
Fig. 4 - The concentration of migrated Fe^{3+} in water over 96 hours / *Concentrația de Fe^{3+} migrat în apă în 96 ore*

amount of Fe^{3+} released by the glass samples over time was investigated, in different environments that can simulate the conditions where soft drinks are kept, namely, distilled water and 10% citric acid solution. Distilled water is the reference medium for the broad spectrum of bottled mineral waters in glass containers, and citric acid is meant to simulate natural fruit juices.

For this test, 2 grams of each glass sample were kept in the mentioned environments, in the dark, in brown glass containers for pharmaceutical use, which hydrolytic stability was previously measured over a longer period of time, and the content of Fe^{3+} was measured at several time intervals.

The determination of Fe^{3+} was done spectrophotometrically, with a UV-VIS Thermo Scientific - Evolution 3000 spectrophotometer, and the method is based on the reaction between Fe^{3+} and ammonium sulfocyanide with the formation of

a ferric thiocyanate complex, coloured in red-cherry, colorimetable at the wavelength of 467 nm.

1 ml of liquid was extracted from the containers at 1h, 2h, 3h, 24h and 96h and a mixture with 2 ml NH_4SCN (40% gr.) and 17 ml distilled water was prepared.

The average values of migrated Fe^{3+} into distilled water from Figure 4 are between 10^{-8}-10^{-9} g/ml, smaller than the value of 0.5 ppm which could affect the quality of a bottled product. [9] A general tendency of Fe^{3+} ion resorption is observed after 1 day of immersion in water, though not all curves have the same trend in the first moments of contact. The random structure of the glass can explain the differences between the amounts of Fe^{3+} that migrate from the glass sample in the first moments. Basically, the probability of finding easy to release ions in the immediate vicinity of the liquid particles is uneven for different samples, and even in the case of two
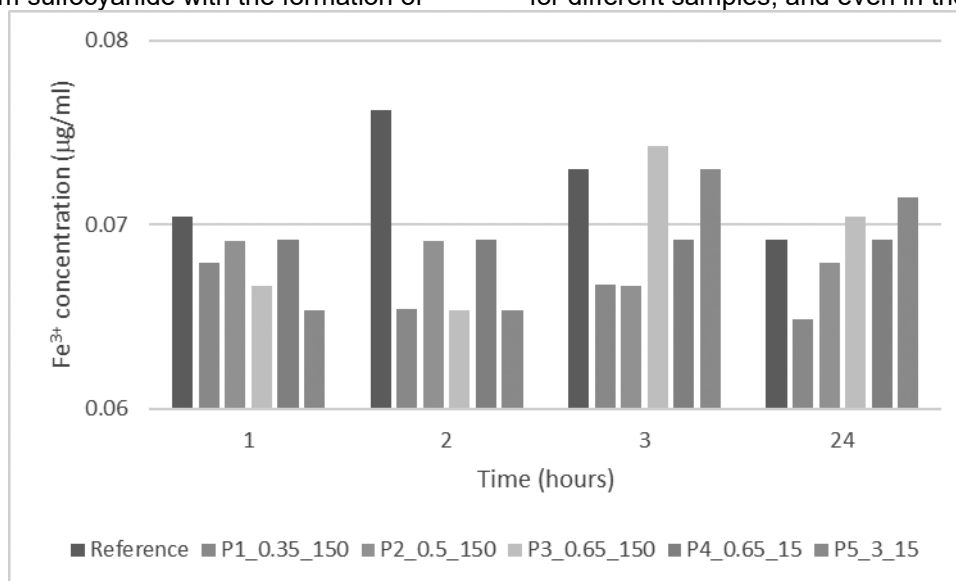

Fig. 5 - The concentration of migrated Fe^{3+} in 10% citric acid solution over 24 hours / *Concentrația de Fe^{3+} migrat în soluție de acid citric 10% în 24 de ore*

samples from the same glass piece. The distribution of the constituent macroanions is so random that it is almost impossible to describe a diffusion mechanism with a predicted velocity.

In the following moments, a kinetic and diffusional equilibrium is established between the ions from solution and those in the glass, the tendency being to bind the iron ions back into the silica gel layer formed on the glass surface. This behaviour has potential applications in the industry, where deferrization treatments are applied in order to stabilize the wine. By a proper modulation of the interaction between the package and the wine, this mechanism could be used in the wine deferral phase, thus making the wine production process more efficient.

Test results for citric acid up to 24 hours are presented in Figure 5.

The same random mode of the iron ions migration is observed in the first minutes, followed by a resorption and a concentration equilibrium

possible interferences greatly limited the scope of the method and subsequently led to the development of new methods based on inductive coupled plasma but introducing mass spectrometry for detection. In the ICP-QQQ working technique, in MS/MS mode of operation, the collision cell between the two quadrupoles can eliminate most of the interference by judicious use of a reaction gas in the collision cell.

For this analysis it was used a 8800 ICP-MS Triple Quadrupole, Agilent Technologies Mass Spectrometer with inductive coupled plasma and laser ablation with concentric nebulizer and Peltier cooling quartz spray chamber in the range -5...+20ºC.

The glass samples obtained in the laboratory were maintained in two liquid environments - 10% citric acid solution and 15% concentration ethyl alcohol solution, for 25 days in the dark at room temperature. From each environment 1 ml of each suspension was

Table 3

ICP-MS results on glass samples kept in citric acid and ethyl alcohol for 25 days / *Rezultatele ICP-MS pe probele de sticlă păstrate în acid citric și alcool etilic timp de 25 de zile.*

Liquid environment	Sample	Na^+ $(mg/l/cm^2)$	Mg^+ $(mg/l/cm^2)$	Fe^{3+} $(mg/l/cm^2)$	Ca^{2+} $(mg/l/cm^2)$
Citric acid 10%	Reference	0.0	0.0	0.0	0.0
	P1_0.35_150	22.9	16.1	10.7	148.2
	P2_0.5_150	9.0	4.7	6.3	47.4
	P3_0.65_150	36.7	5.6	4.1	61.8
	P4_0.65_15	110.5	29.0	31.4	493.5
	P5_3_15	5.6	5.4	2.5	39.7
Ethyl alcohol 15%	Reference	0.0	0.0	0.0	0.0
	P1_0.35_150	0.0	131.0	0.0	118.6
	P2_0.5_150	0.0	165.4	0.0	153.5
	P3_0.65_150	0.0	93.4	0.0	81.8
	P4_0.65_15	0.0	54.9	0.1	69.4
	P5_3_15	0.0	185.3	0.0	175.3

between the solution and the glass sample. In total, the amounts of iron ions migrated in citric acid are of an order of magnitude higher than those in distilled water, thus showing the importance of the pH of the environment in assessing the stability of the glass samples.

3.4. Inductive coupled plasma and laser ablation mass spectrometry (ICP-MS)

This method is used to determine the quantitative elemental composition of various samples, including the trace elements. The inductive coupled plasma ionization technique with optical detection revolutionized the elemental analysis, but the limits of detection and the relatively large number of

analysed. The results are presented in Table 3.

Most of the samples have released in both environments sodium, magnesium, iron and calcium ions, in amounts smaller than those that could change the properties of the products or exhibit toxicity. One can observe differences in the amounts of ions migrated from samples with various compositions or melting time, but also the influence of the liquid environment. For some ions, alcohol caused a significant quantitative release, while for other ions citric acid represented the most corrosive environment.

Because sodium and iron are the chemical elements that could mostly influence the bottled foods, and ethyl alcohol alone does not extract

these ions from the glass, the influence of citric acid on the extraction of these ions from the glass package was considered to be of interest.

As the pH of the liquid medium changes, the solubilization process of the ions from the solid matrix is also intensified, according to the literature data [2, 8, 9]. One can observe the increase of the amounts of sodium and iron ions migrated in the citric acid solution, due to the increased corrosive effect that the solution has on the glass samples.

By analysing the amounts of Na^+ and Fe^{3+} ions released by the five samples after 25 days, it can be noticed the increasing tendency of the concentration of released sodium ions as the melting time changes. As discussed, the attainment of the chemical equilibrium of the glass can also be influenced by the length of time at the melting temperature, influence observed in the case of samples P4_0.65_15 and P3_0.65_150 which have the same oxide composition but the second sample is kept in the oven at maximum temperature 10 times higher than the first. Also, the amount of Na^+ migrated in the liquid medium is significantly higher than that of Fe^{3+} due to the higher mobility of the monovalent ion compared to the trivalent ion, which is more strongly linked in the oxide structure of the glass.

4. Conclusions

The glass containers offer the perspective of controlling the evolution of the properties of the bottled products over time.

In the present study, five different glass samples were obtained, either varying the concentration of Fe_2O_3 in the oxide composition of the samples or changing the time period in which the glass is kept at the maximum melting temperature.

The samples were subjected to tests of thermal expansion, hydrolytic stability and iron ions release in different environments, in order to propose a possible mechanism of interaction of the glass with the products that can be bottled.

The values of the coefficients of linear thermal expansion are in the same range of industrial glass containers, the dilatometric behaviour indicating a correct elaboration and annealing of the samples, comparable with the industrial ones.

The concurrent influence of the maintaining time at the melting temperature and of the iron ions concentration on the stability of samples through standardized methods was observed, they generally having smaller amounts of ions released in distilled water as compared with the industrially produced bottles.

Reaction kinetics in distilled water and citric acid considered over several hours indicate the loss of Fe^{3+} ions from the glass in the first minutes, followed by its resorption (most likely in the silica gel layer formed on the surface of the glass) and a diffusion equilibrium between the two environments is attained. By modulating the interaction of the glass container with the wines, this release-resorption mechanism could be used in the wine deferrization phase, streamlining the wine making process.

Ethyl alcohol does not significantly extract ions from glass, but citric acid does influence the amounts of sodium or iron ions extracted, the ions that can alter, under certain conditions, the organoleptic properties of foods.

The study shows the low capacity of the glass to release toxic or harmful concentrations of ions from its composition, but following a careful research, there is the possibility to develop a dynamic packaging, and thus one can monitor and even control the properties of some glass bottled products.

REFERENCES

[1] Paul, A. Chemistry of glasses. New York : Chapman and Hail, 1982, ISBN 978-94-009-5918-7
[2] Pawel Pohl, What do metals tell us about wine?, TrAC Trends in Analytical Chemistry,. 2007, **26**(9), 941-949, DOI: 10.1016/j.trac.2007.07.005
[3] Esparza Irene, Santamaría Carolina, Fernández J.M., Chromatic characterisation of three consecutive vintages of Vitis vinifera red wine: Effect of dilution and iron addition, Analytica Chimica Acta 2006, **563**(1-2) 331-337, DOI: 10.1016/j.aca.2005.09.043
[4] Krystyna Pyrzynska, Chemical speciation and fractionation of metals in wine, Chemical Speciation & Bioavailability, 2007, **19**, 1-8, DOI: 10.3184/095422907X198040
[5] Nathan R. Perron, Julia L. Brumaghim, A Review of the Antioxidant Mechanisms of Polyphenol Compounds Related to Iron Binding, Cell Biochemistry and Biophysics, 2009, **53**, 75-100, DOI: 10.1007/s12013-009-9043-x
[6] Zongyao Huyan, Shaoxuan Ding, Xiaohui Maoa, Caie Wu, Xiuzhu Yu, Effects of packaging materials on oxidative product formation in vegetable oils: Hydroperoxides and volatiles, Food Packaging and Shelf Life, 2019, **21**, 100328, DOI: 10.1016/j.fpsl.2019.100328
[7] Hae Jin Kim, So Jung Kim, Duck Soon An, Dong Sun Lee, Monitoring and modelling of headspace-gas concentration changes for shelf life control of a glass packaged perishable food, LWT - Food Science and Technology, 2014, **55**(2), 2014, 685-689, DOI: 10.1016/j.lwt.2013.10.018
[8] J. Musgraves, J.Hu, L. Calvez – Springer Handbook of Glass, p. 1234, Ed. Springer Nature Switzerland, 2019, DOI: 10.1007/978-3-319-93728-1
[9] Svenson Anna, Active food packaging- Materials and interactions- a literature review, The Swedish Institute for food and Biotechnology, Karlstad, Sweden, 2004, ISBN: 91-7290-235-3

****