STUDY REGARDING THE INFLUENCE OF METALS MIGRATION UPON THE QUALITY OF BEER AT STORAGE

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Abstract: *For some substances maximum rates of concentration in food and beverages are set. Essential for consumer safety is to study the mechanisms of metal migration in packaging products. Very often, sources of migration are elements of the packaging and this pays scant attention.*
The aim of this work was to determine the content of heavy metals form different kinds of beer from market and to observe: pH of the beer at different periods of time and different temperatures of storage, beer sensorial analysis at different periods of time and different temperatures of storage, physical-chemical properties of beer at different periods of time and different temperatures of storage.
We studied four types of beer for the content of certain metals as Fe, Cu, Cd, Pb, Al and Mn. The test was made at 4°C (for cold beer) and at 20°C for the beer in the shop. For purposes of this study used modern methods and equipment were used. They allow to determine with accuracy the content of various substances in food and beverages.
The results of experimental work showed increased content of various metals. This is the result of migration, which is different for different beers tested. During the preservation period of products in metallic packages, lead and cadmium migration from the packaging material into product takes place with a rate directly proportional with increasing of storage time. The data obtained allow determining the conditions under which drinks are safe for consumers.

Key words: *heavy metals, migration, beer, aluminium can storage*

1. Introduction

The stability of the system food product/ package when food products are preserved in metallic packages is determined by more factors among which the migration of compounds from package into the product preserved holds an important role.
Metallic containers (cans) are often used for food, and in particular for beverage packaging [1]. Most of the beer cans and refreshments are made of aluminium. In comparison with the steel the aluminium and the recipients made of it are lighter more resistant to corrosion easier to mould less resistant in general and more expensive.
All the aluminium recipients have lacquer systems that prevent very well the contact between the food and the metal. In this way all the aluminium levels are generally very low but occasionally they can affect the sensitivity of the products such as beer causing a change of their colour.
The problem of aluminium in beer has been elaborated in several papers over the last decade. However, the effect of aluminium on organoleptic properties of beer has been observed in few papers where it has been stated that aluminium gives beer a »metallic« and bitter flavour

without any observations on particular aroma compound changes.
Also, the number of reports on precise changes of aroma components throughout different storage conditions is surprisingly scarce. [2]
Furthermore, after filling maturated beer into bottles, kegs or cans this process goes on, especially in aluminium cans and kegs. The process of aluminium corrosion and migration from can to beer has been elaborated over the last decade in several papers. The factors of the main influence are: the type and quality of cans, the type and thickness of protective can coating, pH of the beer, the length of contact between the can and the beer, thermal treatment, storage temperature, and presence of any corrosive substances[3].
Although it is well known that dissolved oxygen concentration has decisive influence on beer stability, primary packaging material can facilitate various processes with negative influence on colloidal and/or flavour stability of beer. Beer filled in glass bottles is sensitive to light-struck flavour formation [4]. Canned beer is protected from the influence of light, but aluminium migration from can to beer could aggravate colloidal and flavour stability [5].
Steel beverage can fabrication consists of DWI process, organic application and seaming operation. The seaming operation consists of the junction of body can with the end (can closing). They are widely used as containers of various kinds of beverage. The body of a two-piece can is formed by a draw and wall ironing (DWI) process [1–3]. Overlaying tin on the base steel (tinplate) consists the basic material more used to make food can to conditioner food [4,5].

During end seaming operation, organic discontinuity can be formed at the body hook and at the end hook (internal seam area) caused by small frictions. In the packaging internally lacquered, the interaction product/packing occurs mainly through these discontinuities.
The main consequence of this discontinuity is the iron, which can be dissolved in the food. The reactions involved can modify the flavour characteristic of the product conferring to it metallic flavour. The combination of sensory, nutritional and hygienic characteristics will provide the quality of a food product [6]. For the case of the beverage cans made from tinplate, the control of the migration of iron acquires an even greater importance, because extremely small levels of iron migrated to the drink (0.5 ppm) can already compromise the flavour of the drink [7]. The lacquer coating is the most widely used method for reducing tinplate can corrosion [8-10]. A need for rapid development of new internal coatings on tinplate cans arise in the food and beverage industry, mainly as a response to proposed volatile organic compound regulations [11].

The pressure control is important in achieving the optimal level of carbon gasification of the product and avoiding the excessive creation of foam that leads to the loss of liquid and high air levels in the recipient (affecting the internal corrosion and degrading the quality of the product).

If these technological factors are respected there shouldn't appear in beer any organoleptic or physical-chemical modification when being stored at different temperatures and periods of time [12].

2. Materials and methods

For experiments it was used blonde beer samples on a lot taken from the market. Analyses were conducted periodically throughout six months of storage on for different brands of beer (A, B, C and D brand). Brand A was standard lager beer and brands B, C and D were premium lager beers. Samples were stored in a

refrigerator (4 °C) or in a thermostatic chamber (22°C).
For estimate beer's quality there was made the following methods:

- total acidity determination- the titration method in the presence of phenolphthalein as indicator;
- sensorial analysis- the marking scale method;
- color of beer – observing of view comparison of the analyzed sample's color with the iodine solution's color having a known concentration;
- foam stability – using the times measuring for the persistent foam, starting from the moment when the beer touches the tasting glass till to its total vanishes;
- CO_2 determination – standard method;
- heavy metals content. Prior to heavy metals concentration determination, 40 ml of beer were withdrawn from cans. Containers and laboratory materials were washed with warm, diluted nitric acid and subsequently rinsed with double distilled water (conductivity=0.055 mS/cm). Beer sample was placed in ultrasonic water bath to eliminate carbonation(60 min. at 45Hz, T=20 C, P=100%) and then 5 ml of degassed beer were diluted to 50 ml with 1 % nitric acid (in double distilled water). After wards, the sample was placed in the auto sampler cup and shortly of ICP-MS AGILENT SERIA 7500ce.

3. Results and discussion

3.1. The sensorial analysis- the marking scale method
The results of the appreciations led by the tasting committee members were written in the tasting papers for each sample of beer can presented and then the average percentage was calculated.
On the basis of the average total mark the evaluation of the quality level of beer can samples was led taking on account the organoleptic point of view respectively the place in the quality levels on the 0-20 scale as shown in table 1.

Table 1.
The evaluation of the quality level of the beer can samples analyzed

Samples' name	Total average mark	Mark	Product characterization
Sample A, B, C, D - initially		Very good	The beer can has positive organoleptic traits specific and well determined.
Sample A 1 month	16,5	Good	The beer can has positive organoleptic traits specific and well determined but it presents insignificant taste of heavy metals.
3months	16,3		
6 months	16		
Sample B		Satisfactory	The beer can has organoleptic traits slightly determined and it presents …due to which the product is situated under the standard admitted level for the product.
1 month	15,5		
3 months	14,5		
6 months	12,5		
Sample C		Very good	The bear can has positive organoleptic traits specific and well determined.
1 month	17		
3 months	16,5		
6 months	16	Good	The beer can has positive organoleptic traits specific and well determined but it presents insignificant taste of heavy metals.
Sample D		Good	The beer can has positive organoleptic traits specific and well determined but it presents insignificant taste of heavy metals.
1 month	15,5		
3 months	15		
6 months	14,5		

3.2 Physical-chemical analysis

Foam checking. One of the quality characteristics of the beer appreciated by many consumers is the height of the foam when pouring the liquid into the glass and its persistence. The results of the determinations led are presented in table 3.

Table 3 .
Checking the foam for the superior beer grades analyzed

Sample	Storage time	Foam checking	
		Height of the foam layer [mm]	Foam stability [minutes]
Sample A	1 month	72	15
	3 months	60	12
	6 months	45	5
Sample B	1 month	65	15
	3 months	62	10
	6 months	55	5
Sample C	1 month	70	15
	3 months	64	13
	6 months	48	8
Sample D	1 month	72	15
	3 months	68	11
	6 months	52	7

Table 4.
The physical-chemical properties of the beer at different periods of time and different temperatures of storage

Sample	Storage time (months)	Acidity [ml Na OH/100mL beer]		Co_2 [g/cm^3]		Colour [EBC units]	
		at 4°C	22°C	at 4°C	22°C	at 4°C	22°C
Sample A	1 month	1.8	1.9	0.42	0.46	9.6	9.6
	3 months	2.1	2.2	0.48	0.50	9.8	9.8
	6 months	2.9	3.2	0.52	0.56	9.9	10.2
Sample B	1 month	2.4	2.8	0.68	0.70	10.7	11
	3 months	2.5	3.1	0.72	0.74	10.8	11.7
	6 months	2.9	3.3	0.76	0.78	11.3	12.7
Sample C	1 month	1.9	2.1	0.48	0.51	8.8	9.6
	3 months	2.3	2.4	0.50	0.56	9.8	10.1
	6 months	2.6	2.8	0.52	0.60	10.2	10.6
Sample D	1 month	2.6	2.8	0.69	0.74	10.9	11.3
	3 months	2.8	3.3	0.71	0.78	11.5	11.9
	6 months	2.5	3.6	0.74	0.80	12.3	12.7

3. Heavy metal content

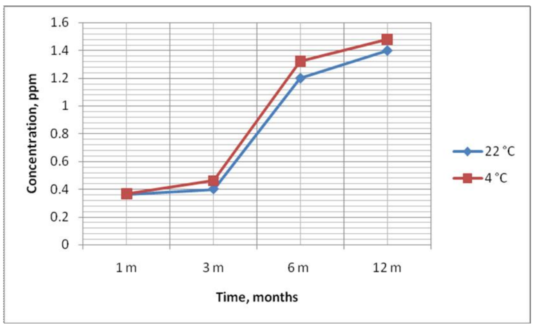

Figure1. Amendment of lead concentration in the product at 4 and 22 degrees- for beer A

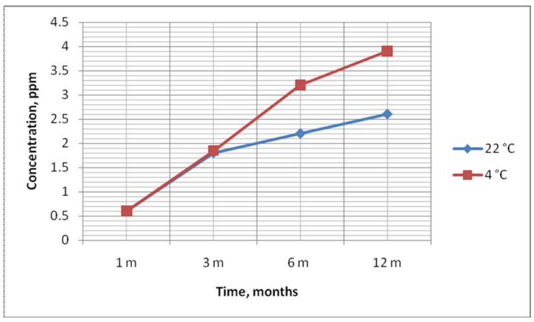

Figure.2. Amendment of cadmium concentration in the product at 4 and 22 degrees- for beer A

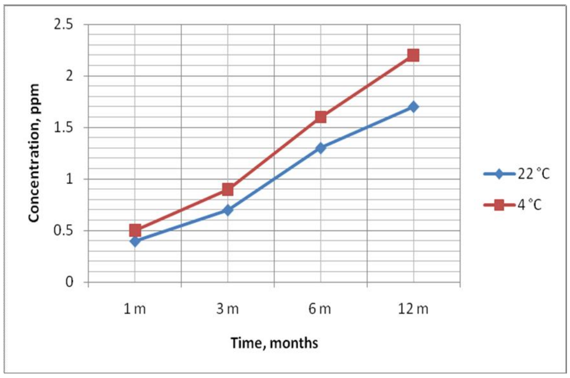

Figure 3. Amendment of lead concentration in the product at 4 and 22 degrees- for beer B

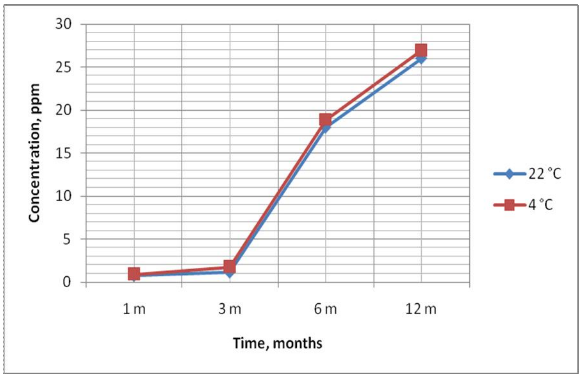

Figure 4.Amendment of the cadmium concentration in the product at 4 and 22 degrees- for beer B

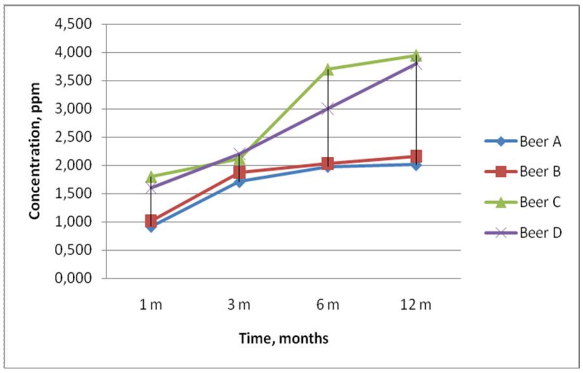

Figure 5. Al content in the product during storage of 4 types of beer

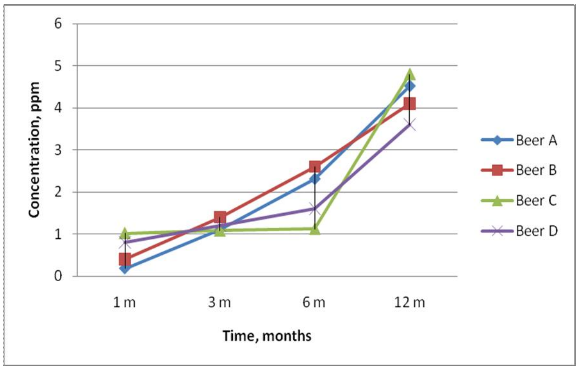

Figure 6. Mn content in the product during storage of 4 types of beer

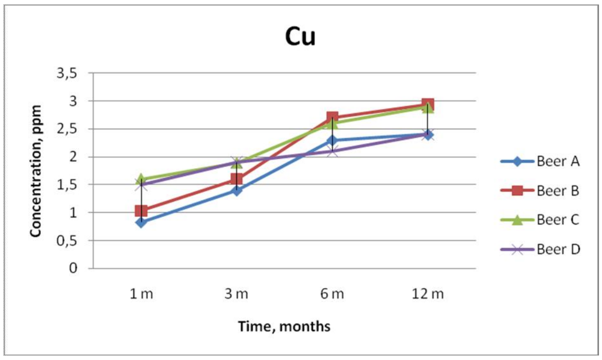

Figure 7 Cu content in the product during storage of 4 types of beer

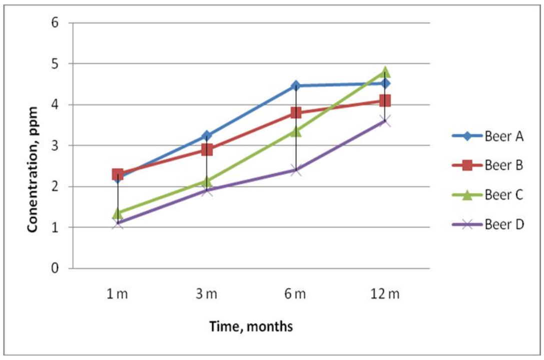

Figure 8 Fe content in the product during storage of 4 types of beer

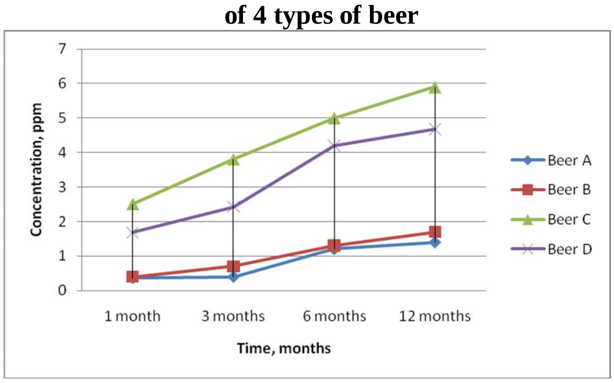

Figure 9 Comparison of lead in different beers

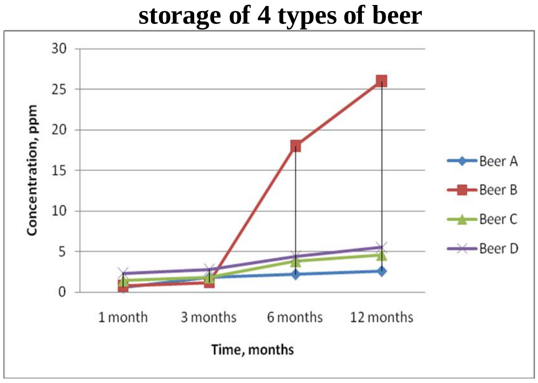

Figure 10 Comparison of cadmium in different beers

4. Conclusion

The results just confirm that heavy metals concentration in finished beer differs among samples of different brands and also among samples of the same brand because heavy metals in beer is derived from various raw materials, equipment and brewing processes. It was assumed that during upside down storage more prominent migration could occur due to the fact that beer is in contact with the edges of the can body and its lid on which more corrosion points could arise.

Generally, temperature of storage influenced heavy metals migration from can to beer. It is obvious that heavy metals vessels in contact with beer have to be well coated to protect the quality of beer. Analyzed samples showed certain aroma stability, which was more expressed for samples stored at 22°C.

Experimental results show that the contents of various metals in beer for the duration of storage. Some beers presence of metals fast rise, which means that any element of the package contains high quantity. Particularly disturbing are the results for the presence of cadmium in beer B. Rapid increase of its content in the product means the wrong choice of one of the elements. With this type of beer is likely at the end of the storage period to exceed the maximum rate of heavy metals from 60 mg/l.

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