STUDY ON THE DEVELOPMENT OF THE MATERIAL BALANCE FOCUSED ON THE METAL TRANSFER BETWEEN THE SYSTEM CAN-LACQUERING AND CANNED VEGETABLES

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Abstract: The paper presents an assessment of the transferable substances amount that is leaking from the packing materials at the food-metallic packing interaction interface by analysing the material balance of the components. The starting point is the theoretical balances of materials. We investigated the transferable materials for rehydrated peas and tomato paste cans. In both cases it was found that an interaction occurs between the organic acids that are found in vegetables as salts and their derivatives, and the metallic structure of the packing material - packaging varnishing system of the can. The real balance of migrated materials gives us an indication concerning the total content of heavy metals accumulated in the cans during the validity period, and allows us to establish precisely a storage period, therefore assuring maximum safety for consumers.
Key words: food safety, material balance, packaging food, canned vegetables

Introduction

In the past years there has been an increasing concern for the food packagings regarding the foods safety due to the possibility of chemical substances migration from the package material in the food stuff. It is known the fact that along with the food stuff the consumer ingests the chemical substances from the packagings and other food contact materials that can migrate into the protected food stuff. The term "migration" usually describes a diffusion process that takes place at the interaction surface between the food and the package, which may be influenced by the compatibility between the food stuff and the packagings and the hygienic quality of the package (Arvanitoyannis & Bosnea, 2004). To insure the food safety by the monitoring of the migration process at the interaction surface between the food stuff and the package has become of a great interest for the entire scientific world. The substances that can affect the human health by migrating from the package into the food undoubtedly depend on the nature of the packaging material (Sendón García & al., 2006).

The substances that leave the package and are transferred into the foodstuff at the interaction surface between the metallic package/ can and the food are of great concern. A correlation between the substances that transfer from the can into the food stuff at the interaction surface between the food stuff and the can be realized by creating a balance of the package material son their components. To create this balance we started with the stoichiometric equation of a chemical process written under the following form:

$$\nu_{A_1} \cdot A_1 + \nu_{A_2} \cdot A_2 + \ldots + \nu_{A_n} \cdot A_n = \nu_{A_1'} \cdot A_1' + \nu_{A_2'} \cdot A_2' + \ldots + \nu_{A_m'} \cdot A_m' \tag{1}$$

In which: ν_{A_i} - the stoichiometric coefficient of the reactants; $\nu_{A_i'}$ - the stoichiometric coefficient of the reaction products: A_i , A_i' - reactants, and reaction products.

At the interaction surface between the food stuff and the package several main and secondary chemical as well as electrochemical reactions take place. To express the quantitative state of the interaction between the food stuff and the metallic can we appeal at a certain moment at *the transformation degree* η_{A_k} *of a valuable or invaluable component* η_{A_i}. This scale is defined as transformed fraction of the valuable component and is expressed by the relation:

$$\eta_{A_k} = \frac{n^0_{A_k} - n_{A_k}}{n^0_{A_k}} = \frac{n^0_{A_i} - n_{A_i}}{\frac{\nu_{A_i}}{\nu_{A_k}} \cdot n^0_{A_k}} = \frac{n_{A'_i} - n^0_{A'_i}}{\frac{\nu_{A'_i}}{\nu_{A_k}} \cdot n^0_{A_k}}$$

(2)

Where: $n^0_{A_i}$, $n^0_{A_k}$, $n^0_{A'_i}$ - is the initial reactional mass composition of the component (A_i), of the valuable component (A_k), and of the reaction products (A'_i); n_{A_i}, $n_{A'_i}$ - the reaction mass composition at a given moment for the reactants (A_i), and for the reaction products (A'_i).

The using of the variable transformation degree for the quantitative characterization of the process allows the development of the stoichiometric calculation in a simple form and the creation of a system of balance equations in a proper form for their using for the quantitative description of the process (Gutt & Gutt, 1993).

The aim of this study was to correlate the substances (metals) quantities that migrate from the package and are transferred into the food stuff at the interaction surface between the food and the metallic can by realizing the materials balance on their metallic components.

Experimental

Materials – The experimental studies and researches regarding the interaction between the food stuff and the metallic can were led on the food products Rehydrated pea and Tomato paste both canned in specific cans made from varnished metallic materials. It was tested a number of approximately 131 cans of each canned product with the dimensions of de Ø 99 x 118 mm and varnished with the following types of lacquers: on the inner can surface - white lacquer PL 1333-16, an don the outer surface - lacquer PL 1014-59 grace. ***Digestion procedures -*** Samples in rehydrated peas and tomato paste cans were prepared by dried mineralization according to the Committee Regulation no.333/2007, using a Berghof equipped with temperature and pressure sensors. ***Instrumentation -*** A Shimadzu Atomic Absorption Spectroscope (AAS) - AA- 6300, equipped with a flame atomization system, electrochemical atomization, hydride generator, autosampler, data acquisition and processing soft was used for the analysis of metals in samples of rehydrated peas and tomato paste cans. Hollow cathode lamps of Cd, Pb, Cu, Fe, Zn and Sn emitting at characteristic wavelengths of the elements (λ_{Cu} = 228.8 nm, λ_{Pb} = 283.3 nm, λ_{Cd} = 324.8nm, λ_{Fe} = 248.3 nm, λ_{Zn} = 213.9 nm, λ_{Sn} = 286.3 nm) were used as the radiation source.

Results and discussion

In the case of the cans with vegetable products - *Rehydrated peas can* and *Tomato paste* can the initial reaction mass is considered to be formed by the organic acids that are present in the vegetables. The organic acids are found in the vegetables as salts and their derivates and influence the taste and preservation of vegetables. The initial reaction mass in the case of Rehydrated peas cans and Tomato paste cans is considered to be formed by metals (lead, cadmium, cooper, iron, zinc and tin) that are part of the structure formed by the metallic material - the lacquering system of the cans and the malic acid from the food product in the case of the peas and the citric acid in the case of the tomatoes. The stoichiometric equations of the chemical processes that take place at the interaction surface between the food stuff and the metallic can are represented by equation (4) in the case of the Rehydrated peas cans and by equation (3) in the case of the Tomato paste cans.

$$Pb^0 + 2Cu^0 + Cd^0 + Zn^0 + Sn^0 + 2Fe^0 + 6C_4H_6O_5 + 4O_2 \rightarrow C_4H_4O_5Pb + C_4H_4O_5Cu + \\ + C_4H_4O_5Cd + C_4H_4O_5Zn + C_4H_4O_5Sn + C_4H_4O_5Fe + Cu(OH)_2 + Fe(OH)_2 + 4H_2O \tag{3}$$

$$Pb^0 + 2Cu^0 + Cd^0 + Zn^0 + Sn^0 + 2Fe^0 + 6C_6H_8O_7 + 4O_2 \rightarrow C_6H_6O_7Pb + C_6H_6O_7Cu + \\ + C_6H_6O_7Cd + C_6H_6O_7Zn + C_6H_6O_7Sn + C_6H_6O_7Fe + Cu(OH)_2 + Fe(OH)_2 + 4H_2O \tag{4}$$

Secondary reaction: $$3Fe(OH)_2 \rightarrow Fe_3O_4 + H_2 + H_2O \tag{5}$$

To express the quantitative state of the interaction reaction between the food stuff and the metallic can at one moment we appealed to the degree of transformation η_{Pb} *of the valuable component or of an invaluable component* $\eta_{C_4H_6O_5}$. The mass of each component at a certain moment is expressed by the equations of the materials balance in table 1:

Table 1. The relations of the materials balance for the components that migrate from the structure metallic material- cans lacquering system into the canned food stuff

Rehydrated peas canned	*Tomato paste*
Entered materials	
$m_{Pb^0} = m^0_{Pb^0} - m^0_{Pb^0} \cdot \eta_{Pb^0}$	$m_{Pb^0} = m^0_{Pb^0} - m^0_{Pb^0} \cdot \eta_{Pb^0}$
$m_{Cu^0} = m^0_{Cu^0} - \frac{M_{Cu^0}}{M_{Pb^0}} \cdot \frac{\nu_{Cu^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0}$	$m_{Cu^0} = m^0_{Cu^0} - \frac{M_{Cu^0}}{M_{Pb^0}} \cdot \frac{\nu_{Cu^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0}$
$m_{Cd^0} = m^0_{Cd^0} - \frac{M_{Cd^0}}{M_{Pb^0}} \cdot \frac{\nu_{Cd^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0}$	$m_{Cd^0} = m^0_{Cd^0} - \frac{M_{Cd^0}}{M_{Pb^0}} \cdot \frac{\nu_{Cd^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0}$
$m_{Zn^0} = m^0_{Zn^0} - \frac{M_{Zn^0}}{M_{Pb^0}} \cdot \frac{\nu_{Zn^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0}$	$m_{Zn^0} = m^0_{Zn^0} - \frac{M_{Zn^0}}{M_{Pb^0}} \cdot \frac{\nu_{Zn^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0}$
$m_{Sn^0} = m^0_{Sn^0} - \frac{M_{Sn^0}}{M_{Pb^0}} \cdot \frac{\nu_{Sn^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0}$	$m_{Sn^0} = m^0_{Sn^0} - \frac{M_{Sn^0}}{M_{Pb^0}} \cdot \frac{\nu_{Sn^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0}$
$m_{Fe^0} = m^0_{Fe^0} - \frac{M_{Fe^0}}{M_{Pb^0}} \cdot \frac{\nu_{Fe^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0}$	$m_{Fe^0} = m^0_{Fe^0} - \frac{M_{Fe^0}}{M_{Pb^0}} \cdot \frac{\nu_{Fe^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0}$

$m_{C_4H_6O_5} = m^0_{C_4H_6O_5} - \frac{M_{C_4H_6O_5}}{M_{Pb^0}} \cdot \frac{\nu_{C_4H_6O_5}}{\nu_{Pb^0}}$	$m_{C_6H_8O_7} = m^0_{C_6H_8O_7} - \frac{M_{C_6H_8O_7}}{M_{Pb^0}} \cdot \frac{\nu_{C_6H_8O_7}}{\nu_{Pb^0}}$
$m_{O_2} = m^0_{O_2} - \frac{M_{O_2}}{M_{Pb^0}} \cdot \frac{\nu_{O_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} =$	$m_{O_2} = m^0_{O_2} - \frac{M_{O_2}}{M_{Pb^0}} \cdot \frac{\nu_{O_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} =$
Out materials	
$m_{C_4H_4O_5Pb} = \frac{M_{C_4H_4O_5Pb}}{M_{Pb^0}} \cdot \frac{\nu_{C_4H_4O_5Pb}}{\nu_{Pb^0}} \cdot m$	$m_{C_6H_6O_7Pb} = \frac{M_{C_6H_6O_7Pb}}{M_{Pb^0}} \cdot \frac{\nu_{C_6H_6O_7Pb}}{\nu_{Pb^0}} \cdot m$
$m_{C_4H_4O_5Cu} = \frac{M_{C_4H_4O_5Cu}}{M_{Pb^0}} \cdot \frac{\nu_{C_4H_4O_5Cu}}{\nu_{Pb^0}} \cdot m$	$m_{C_6H_6O_7Cu} = \frac{M_{C_6H_6O_7Cu}}{M_{Pb^0}} \cdot \frac{\nu_{C_6H_6O_7Cu}}{\nu_{Pb^0}} \cdot m$
$m_{C_4H_4O_5Cd} = \frac{M_{C_4H_4O_5Cd}}{M_{Pb^0}} \cdot \frac{\nu_{C_4H_4O_5Cd}}{\nu_{Pb^0}} \cdot m$	$m_{C_6H_6O_7Cd} = \frac{M_{C_6H_6O_7Cd}}{M_{Pb^0}} \cdot \frac{\nu_{C_6H_6O_7Cd}}{\nu_{Pb^0}} \cdot m$
$m_{C_4H_4O_5Zn} = \frac{M_{C_4H_4O_5Zn}}{M_{Pb^0}} \cdot \frac{\nu_{C_4H_4O_5Zn}}{\nu_{Pb^0}} \cdot m^0$	$m_{C_6H_6O_7Zn} = \frac{M_{C_6H_6O_7Zn}}{M_{Pb^0}} \cdot \frac{\nu_{C_6H_6O_7Zn}}{\nu_{Pb^0}} \cdot m$
$m_{C_4H_4O_5Sn} = \frac{M_{C_4H_4O_5Sn}}{M_{Pb^0}} \cdot \frac{\nu_{C_4H_4O_5Sn}}{\nu_{Pb^0}} \cdot m^0$	$m_{C_6H_6O_7Sn} = \frac{M_{C_6H_6O_7Sn}}{M_{Pb^0}} \cdot \frac{\nu_{C_6H_6O_7Sn}}{\nu_{Pb^0}} \cdot m$
$m_{C_4H_4O_5Fe} = \frac{M_{C_4H_4O_5Fe}}{M_{Pb^0}} \cdot \frac{\nu_{C_4H_4O_5Fe}}{\nu_{Pb^0}} \cdot m$	$m_{C_4H_4O_5Fe} = \frac{M_{C_4H_4O_5Fe}}{M_{Pb^0}} \cdot \frac{\nu_{C_4H_4O_5Fe}}{\nu_{Pb^0}} \cdot m$
$m_{Cu(OH)_2} = \frac{M_{Cu(OH)_2}}{M_{Pb^0}} \cdot \frac{\nu_{Cu(OH)_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta$	$m_{Cu(OH)_2} = \frac{M_{Cu(OH)_2}}{M_{Pb^0}} \cdot \frac{\nu_{Cu(OH)_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta$
$m_{Fe(OH)_2} = \frac{M_{Fe(OH)_2}}{M_{Pb^0}} \cdot \frac{\nu_{Fe(OH)_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta$	$m_{Fe(OH)_2} = \frac{M_{Fe(OH)_2}}{M_{Pb^0}} \cdot \frac{\nu_{Fe(OH)_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta$
$m_{H_2O} = \frac{M_{H_2O}}{M_{Pb^0}} \cdot \frac{\nu_{H_2O_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} = 4$	$m_{H_2O} = \frac{M_{H_2O}}{M_{Pb^0}} \cdot \frac{\nu_{H_2O_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} = 4$

On the basis of the chemical equations and the relations in table 1 we obtained the numerical values for the theoretical materials balance and for the real one for the processes at the interaction surface between the food stuff - Rehydrated peas and Tomato paste - and the metallic package/ the metallic cans during the shelf life. The graphic representations are given in the figures 1, 2, 3 and 4.

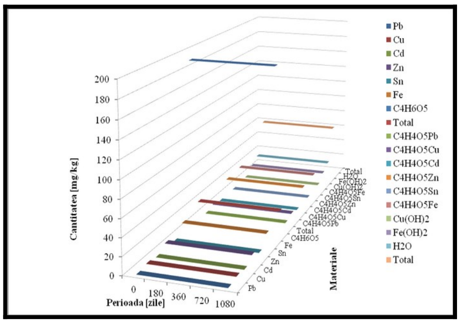

Fig. 1. The theoretical materials balance for the components that migrate from the structure metallic material- cans lacquering system into the Rehydrated peas canned food stuff

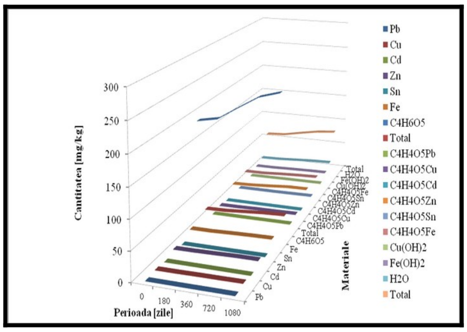

Fig. 2. The real materials balance for the components that migrate from the structure metallic material- cans lacquering system into the Rehydrated peas canned food stuff

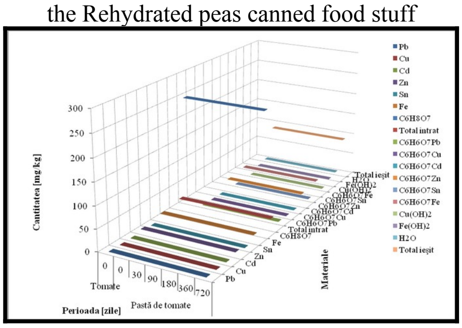

Fig. 3. The theoretical materials balance for the components that migrate from the structure metallic material- cans lacquering system into the Tomato paste canned food stuff

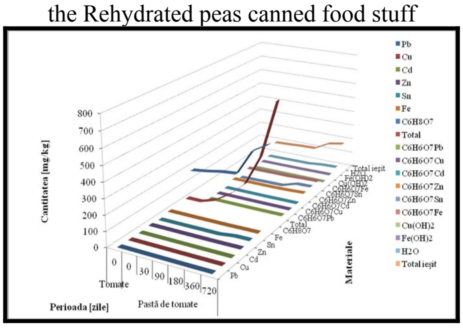

Fig. 4. The real materials balance for the components that migrate from the structure metallic material- cans lacquering system into the Tomato paste canned food stuff

The lead and cadmium are toxic metals that can be very dangerous ingested for a long period of time even at low concentrations. The lead can have negative effects on the peripheric nervous system and can induce severe encephalopathies, and cadmium is accumulated in the liver and kidneys determining kidney dysfunction, skeletal damage and reproductive deficiencies. According to the CF/5 INF/1/2011 Document of Codex Alimentarius Commission, there are traced certain limits for the metallic contaminants in the food stuff: 0.05 – 0.1 mg Cd/kg vegetables and 0.2 – 0.3 mg Pb/kg vegetables; 1.0 mg Pb/kg fruits and canned vegetables, 1.5 mg/kg processed tomato concentrates. Copper is known to both vital and toxic for many biological systems and may enter the food materials from soil through mineralization by crops, food processing or environmental contamination, as in the application of agricultural inputs, such as copper-based pesticides which are in common use in farms in some countries (Onianwa et al., 2001). Zinc is one of the most important trace metals for normal growth and development of humans. The average daily intake has been estimated to be maximally 20 mg Zn/day for adults. It is known that adequate iron in a diet is very important for decreasing the incidence of anemia. Food is the main source of tin for man. Larger amounts of tin may be found in foods stored in plain cans and, occasionally, in foods stored in lacquered cans. The maximum tin level permitted for canned vegetables samples is 250 mg/kg according to the CF/5 INF/1/2011 Document of Codex Alimentarius Commission.

According to the data from the real materials balance, in the case of the two canned products from figure 2 and figure 4 as a consequence of the chemical processes that took place during the shelf life at the interaction surface between the food stuff and the metallic package the levels of their own metals and salts increase in time. An intense increasement of the level of the migration metals from the structure metallic material- cans lacquering system into the food stuff can be observed in a storage period between 180 - 720 days. In this period their can be overpassed the maximum limits admitted for the metals and so the safety of the food stuff can be altered.

Conclusion

In general, the levels of trace metals in canned foods were higher than vegetable samples and it increases during the cans shelf life. The real balance of the migration materials offers us indications regarding the total metals and salts content accumulated in the cans during the products shelf life giving the possibility of action for to obtain and establish a storage period in total safety conditions for the consumers. The work allows concluding that, in order to keep contamination to minimum, canned foods must be consumed in the firsts two months after packaging. The levels may be reduced by more careful handling practices, processing of raw vegetable and using the good quality of packing.

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