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SIMULATION STUDY OF ELEMENT PLASTIC MIGRATION FROM RADIOMETRIC MEASUREMENTS

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ABSTRACT

Element migration from plastic packaging to either foodstuffs or medicine is a serious public health. Many conventional experimental techniques such as chromatography-mass spectrometry, atomic absorption spectroscopy, inductively coupled plasma spectroscopy or calorimetric methods are used to measure total and specific migration of components from plastic packaging. The radiometric method is also used to measure the element migration. In this study a numerical technique was employed to simulate the experimental migration results obtained from measurements of elements from dairy product polymeric packages into 3% acetic acid solution which is a normative food simulant. This numerical technique can be used as complementary tool for the experimental measurements, allowing for a better understanding of the diffusion process and to estimate element migration situations not experimentally measured.

1. INTRODUCTION

The increasing use of plastics in food packaging has led to the need for more information about the interactions between plastic packaging materials and food. Semirigid plastics packaging materials in the form of cups, trays, tubes, vials and bottles (monolayer or multilayer) find a wide variety of applications in the food, pharmaceutical and cosmetic industry [1].

An important radiometric method was established by Saiki and Soares [2] for element migration determination from plastic food packagings to simulating solutions of 3% acetic acid solution and of water. This radiometric method consisted in irradiating plastics with neutrons, followed by exposition for migration and measurement the radioactivity in food simulating solution. The experimental conditions used were 10 days of exposure at 40ºC. The

migration was studied for packagings of water and dairy products. The results indicated the migration of Cd, Co, Cr and Sb to the simulating solutions. The advantages of this methodology are no necessity of blank analysis, as well as the use of high purity simulants. Moreover, it is possible to evaluate the migration to the food contents, instead of simulants. In the conventional methods of migration evaluation, the sample is immersed in a food simulating solution, and the element contaminants that migrate to the simulant are, in general measured by gas chromatography-mass spectrometry, atomic absorption spectroscopy, inductively coupled plasma spectroscopy or calorimetric methods, according to the National Health Surveillance Agency (ANVISA) recommended procedures [3].

Mathematical models are essential for the comprehension of an uncounted number of phenomena. The execution of the model calculus procedure, called *simulation* of the real experiment, at many different phenomenon conditions, could be considered as an experiment inside computer and, generally, is far less expensive then the experiment itself [4]. Diffusion models for migration measurements in food-packaging interactions fit in this case.

In this work we use the mathematical procedure of simulation of [5-7] to simulate many results of Saiki and Soares [2]. It was demonstrated that simulation process give another comprehension perspective of the migration and other information like prevent some results very difficult or impossible to realize.

2. SIMULATION METHODOLOGY

Description of the process is made by the Fick´s second law which, in one dimension, is:

$$\frac{\partial}{\partial t}C = \frac{\partial}{\partial x}\left(D\frac{\partial}{\partial x}C\right) \qquad (1)$$

Where C is the concentration of the migrant, generally in μg/mL, and is a mathematical function which depends on space and on time (x and t), or it is said $C = C(x,t)$. D is the diffusion coefficient. It is x dependent for many systems. Its quantity is $[\text{distance}]^2/[\text{time}]$.

Migration is mass transfer from the packaging into food or medicine by sub-microscopic processes caused by a concentration gradient different from zero. Analogous systems could use the same procedure. As any differential equation, for the solution of eq.(1), it is necessary the initial condition, which is Co = C(x,t=0), and contour conditions. It is common practice to start the study when the concentration is zero into the food or medicine. Starting from Co, C evolves in time, changing its profile or mathematical form, as function of x. Mathematical integration of C(x,tk) in x variable at food (or medicine) results in the quantity of the migrant which passed to the food (medicine) until the time tk. This result is the simulation of experimental kinetic migration essay.

When physical medium where migration took place (x domain) are non-homogeneous, for the precise resolution of eq.(1), D must not be considered constant and can not be putted out of the laplacian (second derivative at 1D). This is the case when interface(s) is (are) present, as in packaging-food systems. For multi-layered plastic packaging this consideration is even more important.

The numerical solution uses a non-uniform mesh of points for the discretization of the x domain. The point density is higher close to the interfaces. In order to numerically solve the Fick´s equation, we discretize the differential eq.(1) by using a three-point finite difference scheme, which is:

$$\frac{d}{dx}D(x)\frac{d}{dx}C(x) \equiv \left(D_{i+1/2}\frac{C_{i+1}-C_i}{\Delta_i} - D_{i-1/2}\frac{C_i - C_{i-1}}{\Delta_{i-1}} \right)\frac{2}{\Delta_{i-1}+\Delta_i} \qquad (2)$$

Δ is the non-constant distance between successive points i.

Numerically, eq.(1) is changed by a trigonal system of n linear equations like eq.(2), where n is the total number of points, solved by the Thomas algorithm [7].

3. RESULTS AND DISCUSSION

The table 1 shows the results of element migration obtained by Saiki and Soares [2] for six samples of dairy product packagings. The migration results are given in terms of element mass that migrated per mass of the simulant solution and area of plastic exposed to migration (ng dm^{-2} kg^{-1}).

Table 1. Elements migration from dairy product packagings (ng dm^{-2} kg^{-1}) to 3% acetic acid simulant.

Packagings	Element	
	Cd	Sb
L2	<57046	<323
L3	<16296	<164
L4	<19516	<152
L5	141598 ± 107	<252
L6	<56911	<287

* The uncertainty was calculated using statistical counting error of standard and of sample

Just one sample presented Cd migration and the Sb migration was not detect in anyone sample. For this study, it was assumed that upper values indicated are the measured values. From migration results, the total mass of each element that migrated to food was calculated. These values obtained for the elements cadmium and antimony were lower than the maximum limit values established in the legislation [8]. The limits are 1.0 mg kg^{-1} for Cd and 2.0 mg kg^{-1} for Sb.

Figure 1 shows the simulation of Cd migration from dairy products packaging into food simulant 3% acetic acid at 40°C and 100°C.

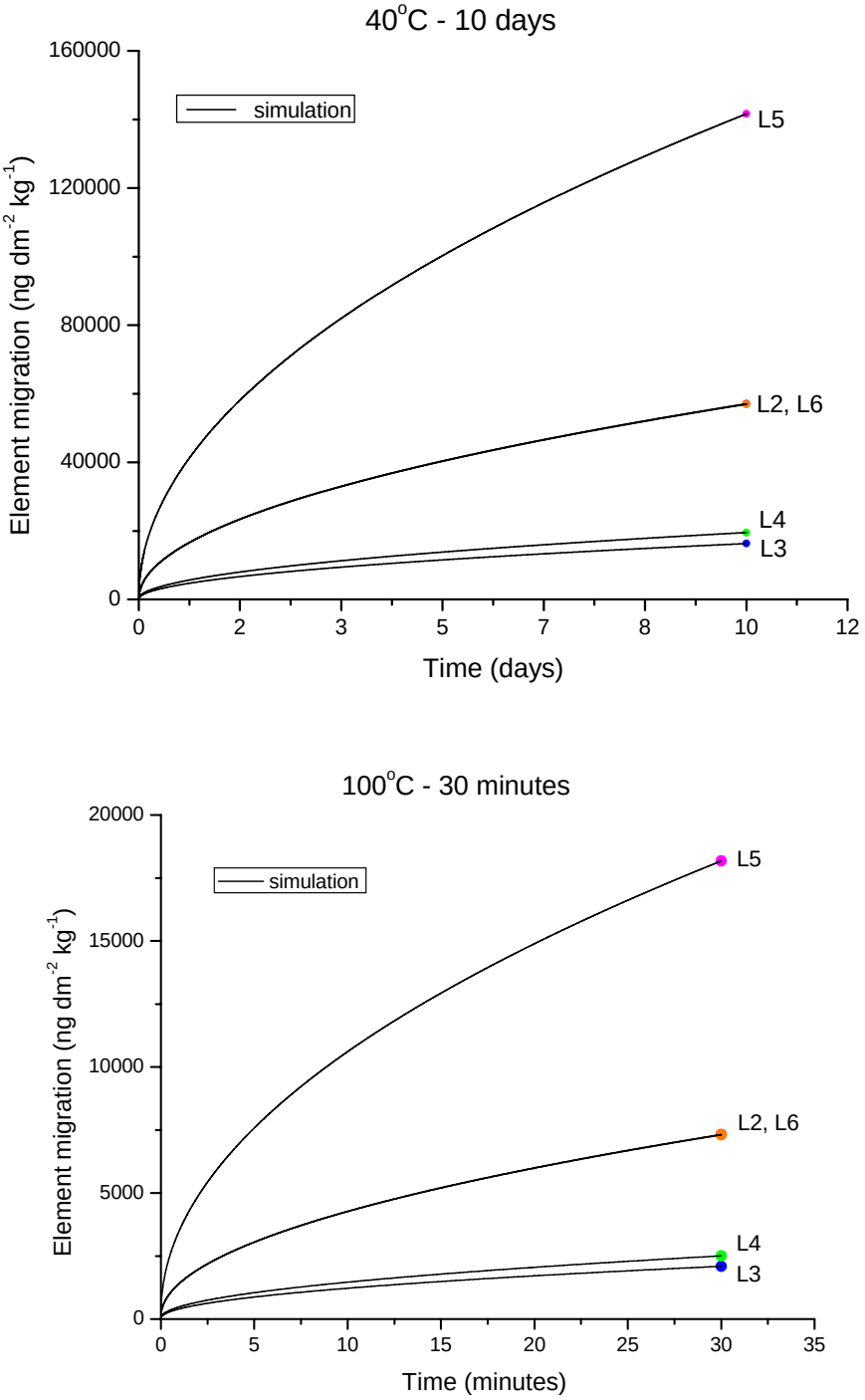

Figure 1. Cadmium migration kinetics from dairy products packaging (L2 to L6) into food simulant 3% acetic acid at 40°C (up) and 100°C (down). Points are experimental results of [2]. Lines are simulation of this work. For 100°C there is only simulation.

Figure 2 shows the simulation of Sb migration from dairy products packaging into food simulant 3% acetic acid at 40°C and 100°C.

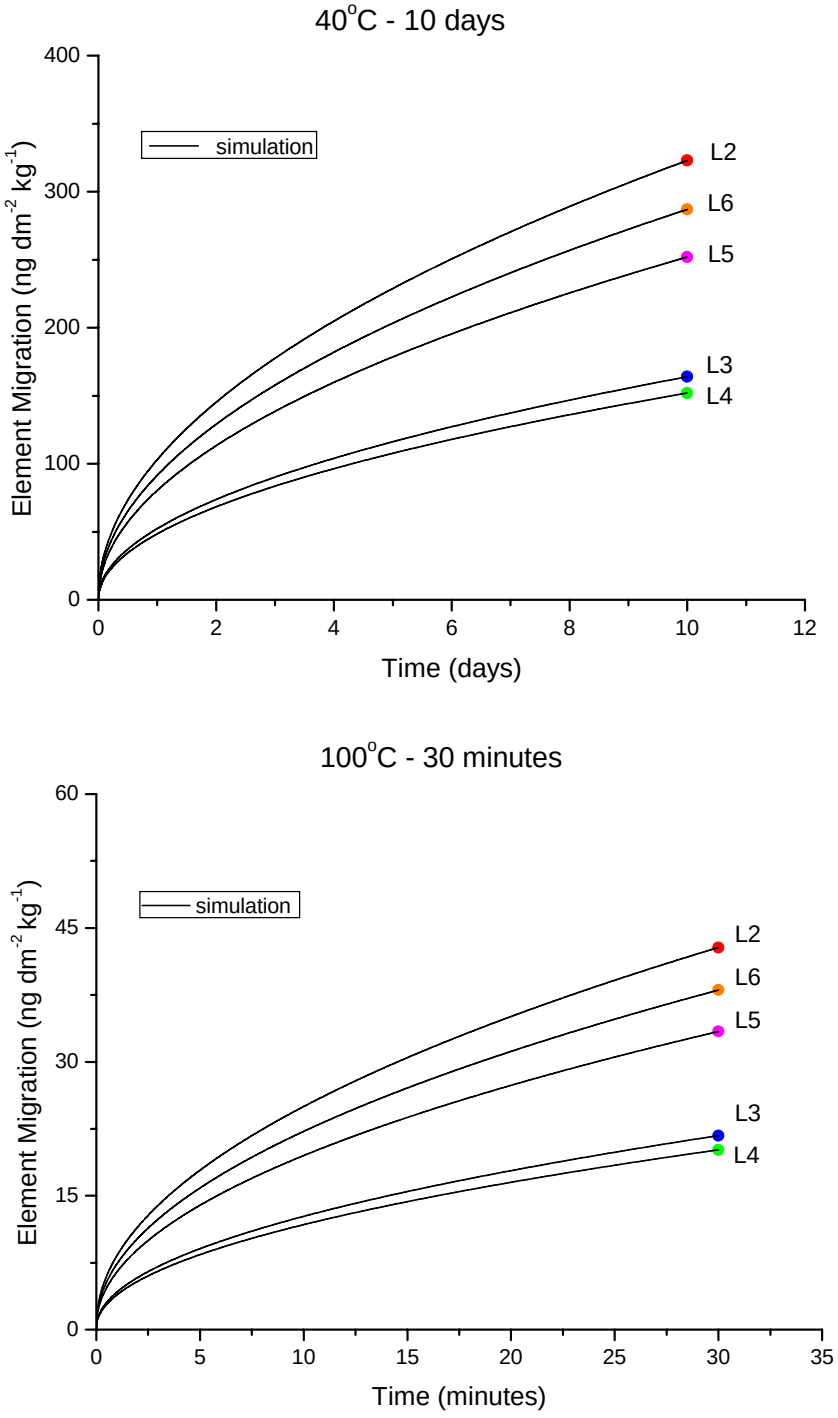

Figure 2. Antimony migration kinetic from dairy products packaging (L2 to L6) into food simulant 3% acetic acid at 40°C (up) and 100°C (down). Points are experimental results of [2]. Lines are simulation of this work.

3. CONCLUSIONS

The simulations of migration kinetics shown fit very well the measured points (or assumed as, when only upper limits do exists) and give an idea of how would be the migration of the elements in any other instant, beside normative ones, even under a different temperature, not measured.

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