XVIII IMEKO WORLD CONGRESS
Metrology for a Sustainable Development
September, 17 – 22, 2006, Rio de Janeiro, Brazil

INITIAL CONCENTRATION PROFILE INFLUENCE ON MIGRATION MEASUREMENTS FROM PLASTIC PACKAGING: A SIMULATION STUDY

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Abstract: Migration of components from plastic packaging into foodstuffs or into medicines is a very important issue, concerning public health. Using experimental techniques, like gas chromatography-mass spectrometry, these essays measure total migration and specific migration of components from plastic packaging. This work presents an explanation and applications of a numerical technique tool for this measurement, allowing the comprehension of the diffusion process and the estimate of component migration in difficult or impractical measurements. As an application example, the non-uniform influence of initial concentration profile on the migration is presented, demonstrating the necessity of this profile determination for high quality considerations on involved metrology.

Keywords: migration, diffusion, packaging, simulation, chemical contamination.

1. INTRODUCTION

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. Diffusion models for migration measurements fit in this case. Description of the process is made by the Fick´s second law which, in one dimension, is:

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

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 [distance]^2/[time].

Migration is mass transfer from the packaging into *food or medicine* (F/M) by sub-microscopic processes caused by a concentration gradient different from zero. Analogous diffusive systems could use the same procedure described here. As any differential equation, for its solution, it is necessary the *initial condition*, which is $C_o = C(x,t=0)$, called here *initial concentration profile*, and the *contour conditions*. Starting from C_o, C evolves in time, changing its profile, or mathematical form, as function of x. An illustration of this behavior is shown in Figure 1.

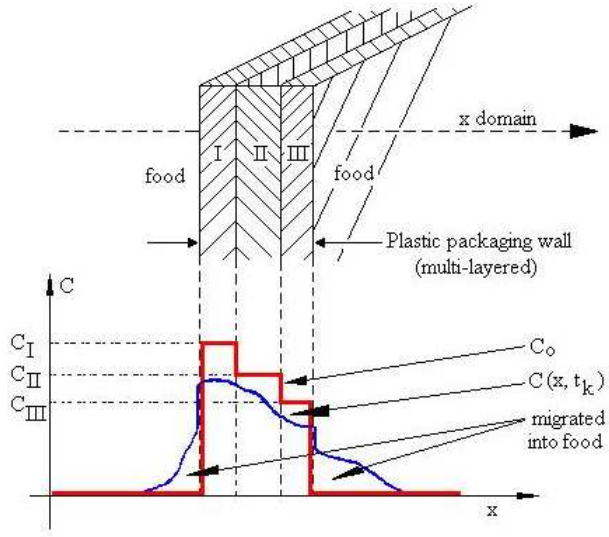

Fig.1: above: sketch of a plastic packaging multi-layer system of three wafers: I, II and III. Below: migration occurs into food at both outside layers as in a typical total immersion migration essay. The initial concentration, C_o, is in red and the concentration profile after a time t_k, $C(x,t_k)$, is in blue. It was not a calculation, it is only illustrative. The area (integrated function) indicated as "migrated into food" is measured in typical migration tests using, as an example, gas chromatography.

Mathematical defined integration of $C(x,t_k)$ in x variable at F/M domain results in the quantity or amount of the migrant which passed to the F/M up to the time t_k. This total

amount of migrant as a function of time is the simulation of experimental migration essay, called *migration kinetic*.

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). This is the case when interface(s) is(are) present, as in packaging-F/M systems. For multi-layered plastic packaging this consideration is even more important. Generally authors use the *partition coefficient* concept [1] to get round this fact, but the theoretical support for this use is not strong.

Many important models had been proposed and used in migration studies, examples are [2-4]. These methods have analytical or numerical solutions, and consider *D* as a constant averaged value, which is putted outside the second derivative. This work presents the numerical method for the solution of (eq.[1]) and the simulation of systems where C_o and *D* can not be homogeneus nor constant in the plastic packaging-F/M system. Here it is presented the influence of this initial concentration profile, $C_o(x)$, on the amount migrated and measured into F/M.

2. METHODOLOGY

The numerical solution uses a non-uniform mesh of points for the discretization of *x* domain. The point density is higher close to interfaces. In order to numerically solve Fick´s equation, it was discretized (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 [5].

3. RESULTS/DISCUSSION

Here it was used generic units for time, [ut], for length (or domain), [us], and for concentration, [C]. Migrated has unit [C].[us]. Typically, [ut] is hour and [us] is micrometer, but it depends on the system.

For a system of monolayer polymer (film of single layer) inside F/M, Figure 2 shows concentration profiles at six different moments from 0 to 1.5 [ut]. At 0 [ut], the concentration profile, C_o, is a sum of three gaussian functions (triple gaussian). This profile could represent a dispersion of some additive caused by package processing, where near outside face of the film it had stood with less migrant than central portion of the film. Figure 3 shows its *migration kinetics*.

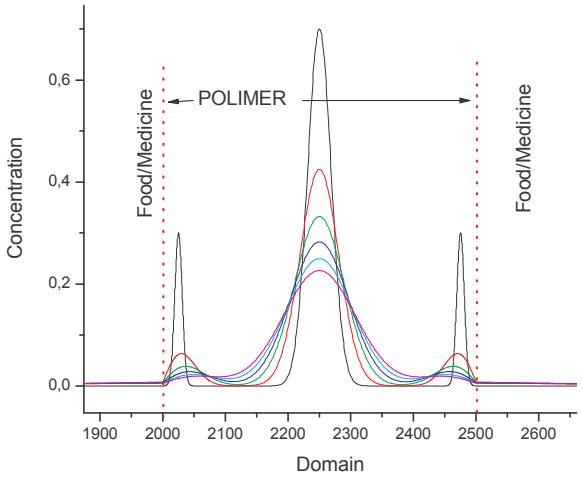

Fig.2: Changes in concentration profiles, due to diffusion, at 0 (black), 0.3 (red), 0.6 (green), 0.9 (blue), 1.2 (cyan) and 1.5 (magenta) [ut]. In this simulation: for polymer, D is 1.10^3 [us]^2/[ut], and for food/medicine, D is 1.10^5 [us]^2/[ut].

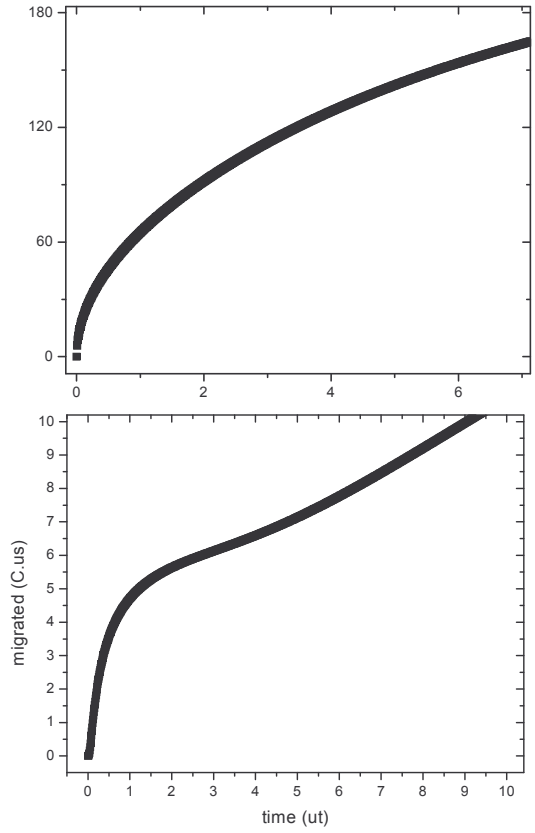

Fig.3: Migration kinetic simulations. Above, quantity migrated as function of time when C_o is a constant mathematical function (not shown) equal to 1.0 [C] only inside de polymer and zero in F/M. Below, result for system of Figure 2. Note the difference in shapes above and below.

Another simulated systems, whose initial concentration profiles are presented in Figure 4, were made with the same amount of migrant inside polymer, for the five different C_o functions shown. We see their very different migration kinetics in Figure 5. It was expected that if a real experiment was conducted in order to quantify the amount of migrant present inside polymer before migration, the results would be the same for all profiles. The total amount of migrant

inside the polymer (TAMP) and the migration kinetic (MK) essays could be measured by gas or liquid chromatography. But it would be very difficult to measure C_o profiles. So, it is quite straightforward to understand the relevance of this simulation if only one of these essays, TAMP or MK, is available.

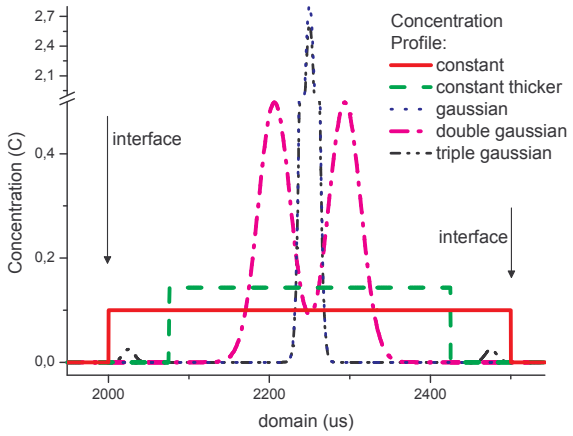

Fig.4: Initial concentration profiles with the same area or integral value. This integral corresponds to total amount of migrant inside the polymer. Interfaces between polymer (2000-2500 [us]) and F/M are indicated. Triple gaussian is a profile where the outside gaussians are smaller than the central one.

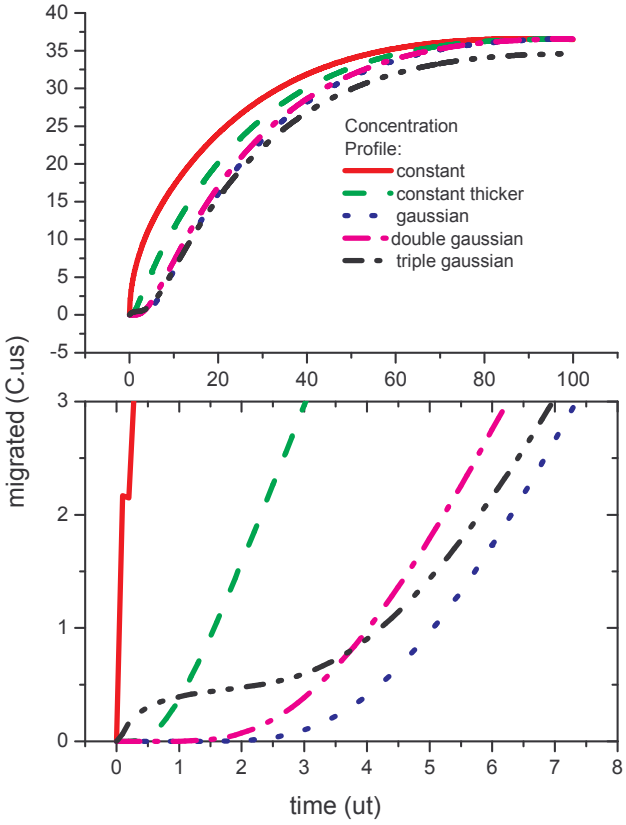

Fig.5: Migration kinetic simulations for each C_o function shown in Figure 4. Graphics above and below differ only in scale.

As a practical application, Figure 6 presents the migration kinetics of Tinuvin P, a U-V radiation absorber additive, from PET bottle, cut as a small sheet and immersed into n-heptane, a food simulant [6]. The agreement of simulation with experiment is very good, and no mathematical model using a constant initial concentration profile could explain the "bump" measured.

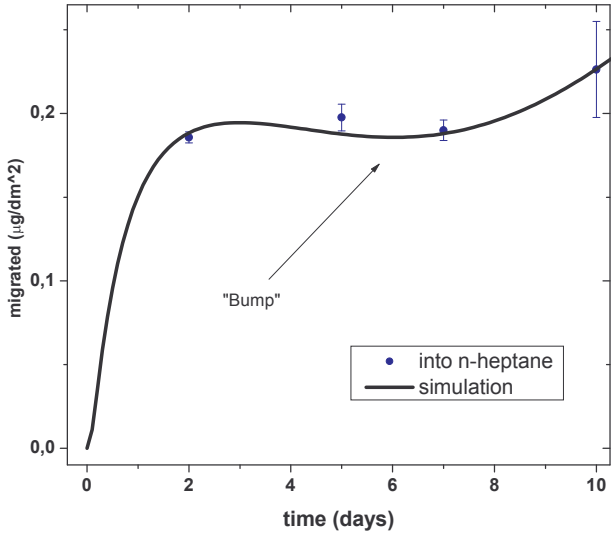

Fig. 6: Experimental results for migration of Tinuvin P into n-heptane and migration kinetic simulation curve (solid) using a triple gaussian C_o profile. Diffusion coefficient of Tinuvin P inside PET was calculated as 4.3 10^2 µm^2/day and inside n-heptane was 5 10^5 µm^2/day.

4. CONCLUSION

It was demonstrated that the *initial concentration profile*, if not constant, even in homogeneous monolayer structures, changes the measurement of migrated components from plastic packaging into F/M. The mathematical shape and values of its migration kinetic curve is affected by this initial profile. If it is not possible to measure this profile precisely, it is important at least to evaluate this profile variation influence and to insert it as a source of uncertainty, in the migration measurement method. This simulation method can be used in this determination of uncertainty component. It can be also used for measurements of diffusion coefficient, limit of shelf life, changes due to temperature, etc.

ACKNOWLEDGMENTS

M. Monteiro and J.S. Félix wish to thank CAPES-PADC/FCF/UNESP (Brazil), for their financial.

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