Accuracy and reliability of different models used for the prediction of the migration from monolayer and multilayer materials

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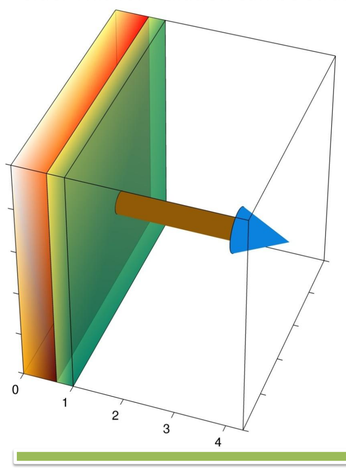
Introduction

Although the EU regulation is still in a consolidation phase, 502 substances (including 230 monomers and 272 additives) among the 937, which are positively listed in EU directives on plastics in contact with food, are subjected to specific migration limits (SML) due to toxicological concern. To face such legal obligations, mathematical modeling, as introduced in article 8 of 2002/72/EC, is a competitive alternative to time-consuming migration tests. **As materials became more sophisticated (multi-layer multi-materials) or as modeling in semi-solid food was required (e.g. for consumer exposure assessment), only numerical techniques were available up to few years via commercial or freely available software**. However, numerical techniques have several drawbacks for end-users with mainly a chemical background: i) they may be computationally burdensome with non-optimized discretization schemes, ii) they may lead to unreliable accuracies for particular stiff problem (e.g. strong partitioning, very thin layers such as adhesive layers), iii) their implementation for legal purposes requires a validation procedure, which is not available. **To tackle the limitations of most of available software, this work addresses new exact analytical solutions i) to validate any migration software, ii) to implement efficient probabilistic modeling, iii) to allow real time calculations and transport coefficients identification.**

Generic mathematical formulation for multilayer materials in contact with a semi-solid food

The canonical solution for the one-dimension migration of packaging substances into a continuously stirred liquid with a finite volume was proposed by Crank [1] with additional refinements discussed by Vergnaud [2]. The first analytical solution for a semi-solid or for a liquid including a mass transfer resistance (i.e. mass Biot or Sherwood number) was proposed by Sagiv [3] twenty-six years later. As the last solution involves a slow convergence with the number of terms, an equivalent but still approximated analytical solution was proposed by Vitrac and Hayert [4]. Very recently, we reformulated the "Sagiv problem" by introducing an efficient mathematical method known as "energy method" already used to solve multi-component convection-diffusion problem to derive exact analytical solutions for problems previously renowned "without analytical solution" [5].

The physical dimensionless formulation is introduced on a comprehensible case consisting in a bilayer material with a whole thickness l_s in contact with a semi-solid food on the right side. This formulation can be straightforwardly downgraded to a monolayer material or generalized to n-layer materials.



Notations (SI units)

A	surface contact area (m)	K_1	Partition coefficient between food and layer 1 (-)
C_f	concentration in food (kg·m^{-3})	K,K_2	Partition coefficient between food and the layer in contact, numbered 2 (-)
C_s	residual concentration in the entire material (kg·m^{-3})	L	dilution ratio = l_s/l_f
$C_1^{t=0}$	initial concentration in layer 1	l_s	whole thickness of the material (m)
$C_2^{t=0}$	initial uniform concentration in layer 2	l_f	equivalent food thickness = V_f/A
c(x,t)	concentration in material at x and t (kg·m^{-3})	t	dimensionless time = $t'\cdot D_2/l_s^2$
Bi	mass Biot number = $h\cdot l_s/D_2$ (-)	t'	contact time (s)
D_1	diffusion coefficient in layer 1 (m^2·s^{-1})	x	dimensionless position (-)
D,D_2	diffusion coefficient in the layer in contact, numbered 2 (m^2·s^{-1})	x'	position (m)
h	interfacial mass transfer coefficient in food (m·s^{-1}), it takes into account the effect of food texture	V_f	volume of food (m^3)
		w_1	relative thickness of layer 1 (-)

Transport equation (dimensionless form)

$$\begin{cases} \dfrac{\partial c}{\partial t}(x,t) = \dfrac{D_1}{D_2}\dfrac{\partial^2 c}{\partial x^2}(x,t) & \text{for } \begin{cases} 0 < x < w_1 \\ t > 0 \end{cases} \\ \dfrac{\partial c}{\partial t}(x,t) = \dfrac{\partial^2 c}{\partial x^2}(x,t) & \text{for } \begin{cases} w_1 < x < 1 \\ t > 0 \end{cases} \end{cases}$$

Contact conditions (dimensionless form)

$$\begin{cases} K_2 \lim\limits_{\substack{h>0 \\ h\to 0}} c(w_1+h,t) = K_1 \lim\limits_{\substack{h>0 \\ h\to 0}} c(w_1-h,t) & \text{for } t > t_0 \\ D_2 \lim\limits_{\substack{h>0 \\ h\to 0}} \dfrac{\partial c}{\partial x}(w_1+h,t) = D_1 \lim\limits_{\substack{h>0 \\ h\to 0}} \dfrac{\partial c}{\partial x}(w_1-h,t) & \text{for } t > t_0 \end{cases}$$

Boundary conditions (dimensionless form)

$$\begin{cases} \dfrac{\partial c}{\partial x}(1,t) = \mathrm{Bi}\cdot C_f(t) - \dfrac{\mathrm{Bi}}{K_2}\cdot c(1,t) \\ \dfrac{\partial c}{\partial x}(0,t) = 0 \end{cases}$$

Exact analytical solutions for **monolayer** materials in contact with a semi-solid food

gradient direction

The **Goujot-Vitrac's solution** expands onto a basis of eigenfunctions, which are orthogonal for a bilinear operator described in [5]. This operator relies on a scalar product, which was optimized to handle a wide range of boundary conditions, such as any arbitrary sorption isotherm and a mass transfer resistance on the food side.

$$c(x,t) = a_0 + \sum_{n=1}^{\infty} a_n \cdot \cos(\lambda_n \cdot x)\exp\left(-\lambda_n^2 \cdot t\right)$$

λ_n are roots of $\tan(\lambda) = \dfrac{Bi\cdot K}{\lambda} + \dfrac{Bi\cdot L\cdot\tan(\lambda)}{\lambda^2}$

$$a_0 = \frac{L\cdot C_s(t=0) + C_f(t=0)}{K+L}$$

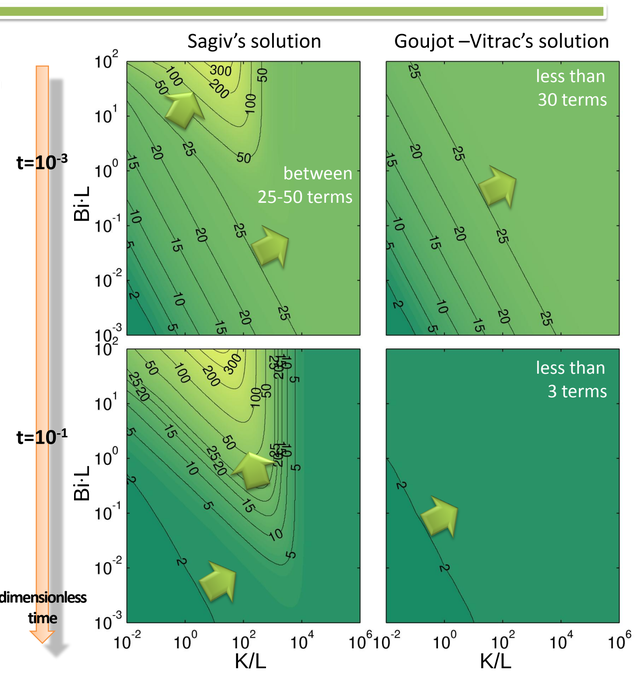
$$a_n = \frac{K\cdot C_s(t=0) - C_f(t=0)}{\dfrac{\lambda_n\cdot\sin(\lambda_n)}{\mathrm{Bi}} + K\cdot\lambda_n\cdot\left(\dfrac{1}{2\cdot\sin(\lambda_n)} - \dfrac{\cos(\lambda_n)}{2\cdot\lambda_n}\right)}$$

It is worth to notice that all solutions are self-similar for any triplet ($Bi\cdot L$, K/L, t)

Number of terms to achieve a maximum relative error in c(x,t) lower than 10^{-5}.

As this criterion is beyond the capabilities of common commercial migration software, it would give the number of terms required to validate a software for any migration condition, that is for any triplet ($Bi\cdot L$, K/L, t).

Only the Goujot-Vitrac's solution [5] guarantees a rapid decrease of the number of terms when the dimensionless diffusion time (t) increases. This property is related to the energy of the solution, which was proven to be strictly decreasing with t. In other words, the high frequency terms vanish rapidly with increasing t, whatever $Bi\cdot L$ and K/L *values*.



Approximated analytical solution for **monolayer** materials in contact with a semi-solid food

Exact solutions suffer from transcendental equations, whose zeros cannot be expressed in terms of a finite sequence of algebraic operations. The **Vitrac-Hayert's solution** derived in [4] solves this issue by approximating the initial set of partial differential equations by a simple conditional ordinary differential equation, while providing an accurate estimate of the mass flux density at the interface. It has been shown that this class of solution has efficient properties to help the identification of transport coefficients from noisy or truncated desorption kinetics.

$$\begin{cases} j = -\dfrac{\partial u}{\partial t} = \dfrac{b}{2}\cdot\left[b - \sqrt{b^2 + 4\cdot c}\right] + c & \text{if } j \ge 6\cdot(1-u); \\ j = -\dfrac{\partial u}{\partial t} = Bi\cdot K\cdot\dfrac{\left(1+\dfrac{L}{K}\right)\cdot u - \dfrac{L}{K}}{1+\dfrac{1}{3}Bi\cdot K} & \text{otherwise.} \end{cases} \quad \text{with} \begin{cases} u(t) = C_s(t)/C_s(t=0) \\ b = Bi\cdot K\cdot\sqrt{\dfrac{3}{2}(1-u)} \\ c = Bi\cdot\left[L\cdot u + (K-L)\right] \end{cases}$$

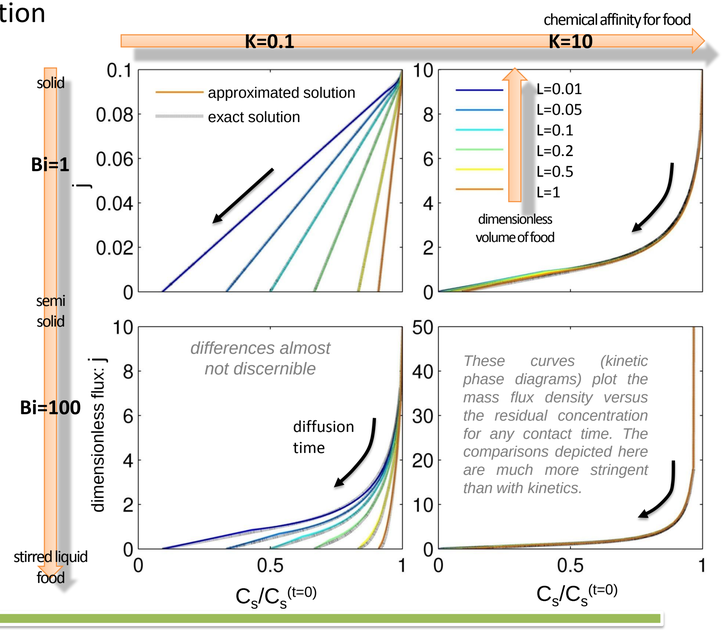
The solution u is obtained by integrating over t: du/dt=f(u)

How accurate is the approximated solution ?

for any contact condition

Vitrac-Hayert's solution leads to accurate results without any bias on residual concentration (C_s) and interface mass flux (j) for any contact condition, while providing an easy numerical implementation in any programming language or even in a spreadsheet.

Combined with a least-square method, it offers real time identifications of combined transport coefficients [4].



Our approach

INRA is contributing to develop basic scientific and engineering supports for a reliable implementation of migration modeling for the packaging community (packaging and food industries, control and regulatory authorities, food safety agencies). As the approach was motivated by Chemical Engineering concepts, our work was concerned with pioneering valuable techniques of prediction from molecular mechanisms to a macroscopic description of food-packaging interactions. Three fields were particularly investigated with possible applications beyond the sole food packaging application:

- **molecular mechanisms** involving in the control of transport coefficients (partition, diffusion coefficients) and in their activation with temperature and plasticizing effects;
- **exact mathematical solutions of transport equations** for punctual assessment and probabilistic assessment of the contamination of food products by materials intended to be in contact;
- **design of decision tools**, which act as expert systems and which can handle both missing properties and large uncertainties on input parameters.

Free implementation of last algorithms and methodologies on the SAFE FOOD PACKAGING PORTAL: http://h29.univ-reims.fr

Exact analytical solution for **multilayer** materials in contact with a semi-solid food (the first exact solution ever published)

An exact solution for multilayer materials has been recently derived [6] from the generalization of the scalar product defined in [5]. The solution expands on a basis of eigenfunctions, which depends on the considered layer. For concision, the solution for a bilayer material is presented here.

$$c(x,t) = a_0 + \sum_{n=1}^{\infty} a_n \exp\left(-\lambda_n^2\cdot t\right)\cdot\begin{cases}\cos\left(r\cdot\lambda_n\cdot x\right)/g_n & \text{if } x < w_1 \\ \cos(x\cdot\lambda_n + f_n) & \text{if } x > w_1\end{cases}$$

λ_n are roots of $\tan\left(\arctan\left(\dfrac{\lambda^2/\mathrm{Bi} - L}{K_2\cdot\lambda}\right) + (1-w_1)\cdot\lambda\right)\cdot K_2\cdot\tan(r\cdot w_1\cdot\lambda) = K_1\cdot r$ with $r = \sqrt{\dfrac{D_2}{D_1}}$

$$a_0 = K_1\frac{w_1\cdot L\cdot C_1^{t=0} + (1-w_1)\cdot L\cdot C_2^{t=0} + C_f(t=0)}{w_1\cdot L\cdot K_2 + (1-w_1)\cdot L\cdot K_1 + K_1\cdot K_2}$$

$$a_n = \frac{2}{b_n}\cdot\left(\left(K_1\cdot C_1^{t=0} - K_2\cdot C_2^{t=0}\right)\cdot\sin(\lambda_n\cdot w_1 + f_n) + \left(K_2\cdot C_2^{t=0} - C_f(t=0)\right)\cdot\sin(\lambda_n + f_n)\right)$$

$$b_n = \left(\frac{L}{\lambda_n} + \frac{\lambda_n}{\mathrm{Bi}}\right)\cdot\sin(\lambda_n + f_n)^2 + \frac{D_1\cdot K_1\cdot\lambda_n\cdot w_1}{D_2\cdot g_n^2} + K_2\cdot\lambda_n\cdot(1-w_1)$$

$$f_n = \mathrm{atan2}(K_2\cdot\sin(r\cdot w_1\cdot\lambda_n), r\cdot K_1\cdot\cos(r\cdot w_1\cdot\lambda_n)) - \lambda\cdot w_1$$

$$g_n = \sqrt{\left(\frac{K_1}{K_2}\cdot\cos(r\cdot w_1\cdot\lambda_n)\right)^2 + \sin(r\cdot w_1\cdot\lambda_n)^2\cdot\frac{D_1}{D_2}}$$

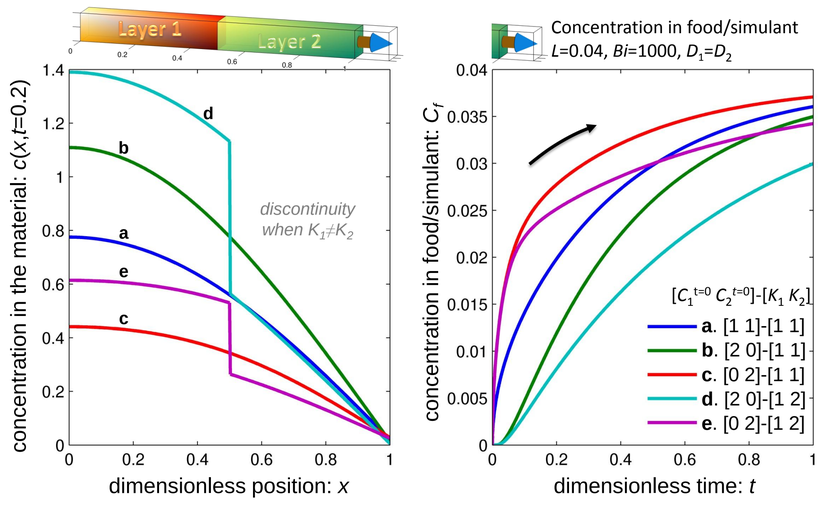
$$\mathrm{atan2}(y,x) = \begin{cases}\dfrac{\pi}{2}\cdot\mathrm{sgn}(y) - \arctan\left(\dfrac{x}{y}\right) & y \ne 0 \\ \dfrac{\pi}{2}\cdot\mathrm{sgn}(x) - \dfrac{\pi}{2} & y = 0\end{cases}$$

Illustration on a bilayer material

How does the analytical solution expands over several layers ?

The example illustrates four practical cases with a same initial amount of migrant in the entire packaging. The scenarios are coded by the paired values: [$C_1^{t=0}$ $C_2^{t=0}$]-[K_1 K_2]:

(**a**) monolayer,
(**b**) material including a functional barrier
(**c**) bilayer including similar materials,
(**d-e**) bi-materials.



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