Modelling migration in multilayer systems by a finite difference method: the spherical symmetry case

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Abstract. We present a numerical model based on finite differences to solve the problem of chemical impurity migration within a multilayer spherical system. Migration here means diffusion of chemical species in conditions of concentration partitioning at layer interfaces due to different solubilities of the migrant in different layers. We detail here the numerical model and discuss the results of its implementation. To validate the method we compare it with cases where an analytic solution exists. We also present an application of our model to a practical problem in which we compute the migration of caprolactam from the packaging multilayer foil into the food.

1. Introduction
Migration of substances from packaging to foods is an important issue for the industry due to the consumer protection regulations enforced by many industrialized countries (for example in the EU Regulation 10/2011 or the FDA regulations in the USA). The main concern is the existence of a dangerous chemical agents in the multi-layer packaging which migrate from one of the layers into the food affecting consumers’ health. Migration can be determined experimentally and/or estimated by using appropriate theoretical models which allow the calculation of the migrant concentration in the food under specific contact conditions with the packaging. The development of such models allows estimating the migrant concentration in the product instead of performing costly laboratory tests. Modeling also helps laboratories to understand the physical and chemical processes behind the measured data and to estimate material parameters like diffusion and partition coefficients.

The migration model is essentially based on the diffusion equation assisted by partitioning: the ratio of migrant concentrations in two adjacent layers is imposed by the ratio of the migrant solubility in the two layers. Finite difference, finite element, finite volume, boundary element and semi-analytical methods have been developed to handle this problem (see [1] for a review). In particular finite difference methods proved to be simple enough to be suitable for planar geometries [2-4] and were used to model packaging with plastic foils as well as for cylindrical geometries which were developed to model cylindrical packaging [5] and water pipe cases [6].

A different problem is related to the study of the so-called master-batch additives. In this case the plastic foil which will subsequently used to pack the product is treated with chemical agents with the aim of modifying some of its properties (such as UV resistance, stiffness, scent,
etc.) or color. The migrant is initially incorporated into tiny granules which are then added to the final plastic product. The substance starts to migrate from the spheres and slowly diffuses into the plastic until it reaches a uniform concentration.

In this paper we apply a finite difference method to solve the migration problem for spherical geometry in a multi-layer configuration. We will formulate the problem and present the method used for solving it in section 2, while in section 3 we validate the procedure as we compare it to the analytical form. In the last section we draw the conclusions and suggest further developments and tests for our method.

2. The model
The problem presentation starts from Fick’s law of diffusion: for a concentration whose spatial profile is known at \( t = 0 \), the equation gives the concentration at time \( t \) given the diffusion coefficient \( D \).

\[
\frac{\partial c}{\partial t} = D \nabla \cdot (\nabla c) \tag{1}
\]

Transforming into spherical coordinates and assuming isotropic medium for all directions of \( r \) we get the equation for our model:

\[
\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) \tag{2}
\]

To solve the diffusion equation numerically we perform the following steps: (i) we define a non-uniform numerical grid (ii) we use Lagrange polynomials to approximate the differences at mesh points; (iii) we discretize the diffusion equation using finite differences; (iv) eventually we solve the resultant system of algebraic equations, having the following form:

\[
-\theta_{i-1} g_{i-1} c_{i-1}^{n+1} + (1 - \theta_{i-1}) g_{i-1} c_{i-1}^{n+1} - \theta_{i+1} g_{i+1} c_{i+1}^{n+1} = -\bar{\theta}_{i-1} g_{i-1} c_{i-1}^n + (1 - \bar{\theta}_{i-1}) g_{i-1} c_{i+1}^n - \bar{\theta}_{i+1} g_{i+1} c_{i+1}^n, \tag{3}
\]

with \( c_i^n \) representing the concentration of the migrant for the mesh point \( i \) and time \( n\delta t \). The \( g_i \) coefficients are obtained from the Lagrange polynomials.

Discretization also implies deriving the equations at the interface between adjacent layers (dependent on the partition factor), as well as for boundary conditions. The partitioning between two adjacent layers \( i \) and \( j \) impose that the concentration \( c \) at the interface obeys the condition \( k_{ij} = c_i / c_j \). The algebraic equations for these grid points were obtained by applying the fictitious point method as described in \([7]\). The model was implemented on a computer program and compared with the analytical solution given by \([8]\) for a particular case of initial and boundary conditions. The validation is presented in the next section.

3. Testing and Results

3.1. Validation
The next step was to validate the numerical method used to solve the diffusion problem. To do this we found cases in which the problem is analytically tractable, for example in Crank’s book \([8]\) for different initial and boundary conditions. We choose the case of migration from a well-stirred solution into a medium which surrounds the sphere uniformly and symmetrically. The case corresponds to a migration in a two-layered configuration with a partition coefficient \( K \) between them. We consider the sphere with a uniform distribution of concentration \( C_0 \) and the surrounding medium free of migrant.

The expression for the amount of migrant at time \( t \), as a fraction of the mass found at in infinitely long period of time \( M_\infty \) is given by the following equation:
\[
\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha + 1)\exp[-Dq_n^2t/a^2]}{9 + 9\alpha + q_n^2\alpha^2},
\] (4)

where \(q_n\) are the non-zero roots of the equation

\[
\tan(q_n) = \frac{3q_n}{3 + \alpha q_n^2}.
\] (5)

Although (4-5) require numerical methods to find the roots and to sum up the series, in the following we will refer to it as the analytical solution.

The parameter \(\alpha = V_{\text{medium}}/(K \cdot V_{\text{sphere}})\) represents the ratio of the volumes of the medium and the sphere taking into account \(\alpha\). The partition coefficient \(K\) has the significance that the concentration of the migrant found in the surrounding medium at the interface with the sphere, is \(K\) times the concentration found in the sphere at the interface between the two layers.

**Figure 1.** Relative error as a function of \(Dt/a^2\), for different values of \(\alpha\) up to large period of time.

**Figure 2.** Relative error between analytical and numerical results, as a function of the parameter \(\alpha\), computed for large values of \(t\).

We calculated numerically and analytically the total quantity of migrant found in the surrounding medium as a function of time \(t\). The other parameters are \(a=1\ cm\) (the radius of the sphere), \(C_0=10\ ppm, D=10^{-9}cm^2/s\). In general we obtained a very good agreement between the numerical and analytical results although the earlier the time the larger the difference in concentration. This aspect is illustrated in more detail in figure 1 where we represent the relative error (in absolute values) between the two sets of data for different values of \(\alpha\). One can note a decrease of the relative error towards a stable value as the time increases to very large values. One can see a cusp in the case where we chose the partition coefficient \(\alpha = 25\) which occurs due to a change of sign of the error.

Since figure 1 contains the curves for different values of \(\alpha\) we can plot directly the dependency of the error on \(\alpha\) at a given time. We illustrate this in figure 2 where it can be clearly seen how the value of \(\alpha\) affects the relative error of the two cases. For \(\alpha\) values up to 10 the error values are of order \(10^{-3}\) while as \(\alpha > 10^2\) the relative error becomes insignificant, with values very close to zero. The plot is made for time value chosen as \(t = 3 \cdot 10^5\) hours.
3.2. Application to food packaging
The migration module was integrated into the FP7 program “Flavorings, Additives and Food Contact Materials Exposure Task” (FACET) with the role of computing the quantity of migrant that ends up in food from food contact materials, especially packaging. The presented model development is dedicated to spherical symmetry which can be found in various food packagings (cheese, chocolate, etc.)

As an example we present here the migration of caprolactam from a 3-layered polymer packaging composed of polyamide (PA), glue and polyethylene (PE) into the food sample (in this case, Gouda cheese).

Figure 3. Amount of caprolactam found in cheese at different periods of time, for 6°C (shelf temperature) and 20°C (room temperature).

Caprolactam is a chemical compound having the chemical formula \((CH_2)_5C(O)NH\). It is used as an additive in plastics and polymers, and in the practical case it is initially found in the external layer made of polyamide. The maximum allowed concentration of caprolactam in food, as indicated by the European directive 2002/72/EC, is 15 mg/kg in food.

Figure 4. Spatial profile of the concentration in cheese and packaging foil after 90 days.

Figure 5. Detailed spatial profile of the concentration for the cheese/packaging interface.
The values for partition and diffusion coefficients were estimated from measurements or, when not available, from the Piringer formula [7]. We estimated the migration at 6°C (shelf temperature) and 20°C (room temperature). The results are illustrated in figure 3, showing the variation in time of the caprolactam concentration in food. We see that for both temperatures the final concentration after 90 days is lower than the specific migration limit (SML).

If we analyze the spatial profile of caprolactam concentration in food, see figure 4 and figure 5 we note that for regions in contact with the packaging, SML in cheese is exceeded, reaching more than 20 ppm after 7 days of migration. This result shows the utility of the numerical modeling as one can estimate the amount of food in which SML is exceeded while the laboratory experiments give only the average amount of caprolactam extracted from the food.

4. Conclusions
In this paper we presented a numerical model based on finite differences to solve the problem of chemical impurity migration within a multilayer spherical system. A practical application of this model is in the case of chemical species migration from polymer packaging into food products.

In conclusion, we can state that the model is well suited to simulate the migration from spherical objects in multilayer systems, as it can be seen from the error plots and the scenario for foil migration. Due to the difficulty and limited possibilities of the analytical treatment, this numerical model is more flexible regarding the parameters of the real system such as diffusion and partition coefficients or layer thickness, and it has the advantage that it can be generalized to an arbitrary number of layers.

The model can be further extended to incorporate time and space dependent diffusion coefficients as well as time dependent partition coefficients. For the planar geometry it was integrated in the FACET software [9] which calculates the exposure of the European customer to the chemicals found in food contact materials, in particular packaging. Including cylindrical and spherical geometries is also intended.

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