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A comparison between experimental results and a mathematical model of the oxidation reactions induced by radiation of ferrous ions

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Abstract

The dependence of the response of chemical dosimeters as a function of the irradiation temperature is an important issue that has not yet been addressed within a mathematical modeling framework. The temperature dependence of the dose–response function has to be taken into account in practical applications, mainly in frozen food sterilization by radiation. Significant errors may occur if the dependence of the dosimeter response on the irradiation temperature is not taken into account properly. The experimental results obtained irradiating iron salt solutions at different temperatures below and above 0 °C show that the change in the valence of Fe^{2+} as a function of dose are linear for both liquid and frozen solutions. This led us to conclude that the iron salt solution seems suitable for low-temperature applications having a linear dose–response up to 600 Gy, despite a progressive decrease of sensitivity as temperature decreases. A nonlinear differential model for the kinetics of reactions induced by radiation in iron salt solutions was established. In the model a temperature correction factor was included in order to take into account abrupt changes observed in the kinetics of the chemical process when the irradiated solution's allotropic phase changes from liquid to solid (ice). Fitting the kinetic model to the experimental results at different temperatures we found the temperature correction factors.

Keywords: Mathematical model; Frozen solutions; Irradiation; Temperature; Iron salts

1. Introduction

Low temperature irradiation is important in areas such as the preservation of some commercial products and space research. Astrobiology is one of the branches of space research where experiments simulating extraterrestrial conditions are commonly performed. In recent years, such experiments have been carried out simulating different extraterrestrial icy bodies, e.g., comets (Negrón-Mendoza et al., 1995). Chemical reactions are induced by the radiation of cosmic rays entering the icy bodies. In the laboratory, in the simulated experiments, the evaluation of the deposited energy is an important factor that needs to be determinate. During experimental simulation studies, dose measurements can indicate the amount of energy deposited by the radiation and can do so accurately using means provided by radiation chemistry. With these measurements, one can develop a quantitative picture of the changes induced by ionizing radiation in the samples.

On the other hand, the possible use of frozen solutions as dosimeters must be based on the experience accumulated on the irradiation of water and aqueous solutions. The radiolysis of water has been an important research area in radiation chemistry and became essential for the understanding of the radiolysis of aqueous solutions (Draganic and Draganic, 1971). Nevertheless, evaluating the energy deposited by gamma radiation on samples irradiated below room temperature is sometimes a very difficult task. With this we have the advantage of keeping in mind the well-known condition that the dosimeter and sample should bear as much as possible the same irradiation conditions.

Chemical reactions induced by radiation in aqueous solutions are the basis of chemical dosimeters. When water is activated by radiation it does decompose in very reactive species that induce chemical reactions in the system. The term "activated water or ice" is used to describe water or ice that has been irradiated.

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Chemical analysis has been used to deduce the reactions taking place in the samples rising from the decomposition of liquid water, as well as pulse radiolysis and competition kinetic methods were used to evaluate a great number of rate constants involved (Draganic and Draganic, 1971).

In this paper we report the irradiation of iron salt solutions with gamma rays at different decreasing temperatures, keeping constant the rest of the irradiation conditions. For temperatures below the freezing point we assume that we have in the frozen solution an "activated ice". It is well known that the response of this kind of dosimeter is determined by the change in valence of Fe^{2+} to Fe^{3+}.

We were interested in investigating whether the experimental dose–response function, which shows an abrupt slope change when the temperature decreases below 0 °C, can be reproduced satisfactorily with a corrected kinetic model. The model consists of a system of nonlinear differential equations describing the kinetics of the chemical reactions in the irradiated iron salt solution. Based on our experimental results, such factor was expected to be a strictly decrescent function of the irradiation temperature.

Therefore, this article is concerned with the implementation of a computational framework for a mathematical model of reactions induced by radiation via water radiolysis for simulating the irradiation process, as well as for computing the correction factor by fitting experimental results.

2. Methods

2.1. Translation from chemical reactions to differential equations

The chemical reaction equations are expressed in the source code of the program written in C^{++}, using a nomenclature very similar to that used by chemists. The program contains a translation part that, by analyzing the reaction equations, constructs a vector containing the concentration of the chemical species at discrete integration steps and stores the corresponding reaction constants in a two-dimensional matrix form. With the source terms, corresponding in this case to yield by radiolysis, a vector is filled. The information contained in the vectors at a time instant t and in the reaction constant matrix allows computing the right-hand side (RHS) of the differential system and the Jacobian for the system. After that, using an integration scheme it is possible to predict the concentrations at a future time $t+\Delta t$.

2.2. Balance equations

The accurate solution of the differential equation system describing the chemical reactions requires an overall conservation of the mass balance. Two main factors are involved in the conservation of mass, namely the reaction mechanism and the integration process. However, it must be pointed out that the formal stoichiometric balance need not be the same as with atomic balance. The program recognizes each species as a name, and the individual letters and numbers in the name are of no significance in the balance continuously. It is sufficient to do that at the start of the integration, i.e., at time $t = 0$. The dependent variables of kinetic models are the molar concentration of the chemical species $\chi_m(x,t)$ for $m = 1, 2, \ldots, n$ where n is the number of species, x is the spatial coordinate defined in a reference system on the irradiated sample and t is the time.

Table 1
An enumeration of the chemical species considerated in the kinetic model and its initial concentrations

Specie number	Specie	Initial concentration
1	Fe^{2+}	1.6E − 03
2	H	0.0
3	O_2	1.2E − 02
4	e_{aq}	0.0
5	H_3O^+	4.0E − 01
6	Fe^{3+}	0.0
7	OH	0.0
8	H_2O_2	0.0
9	HO_2	0.0
10	HO_2	0.0

To solve the kinetic system, a proper set of initial concentrations of all the species must be given. We considered H_3O^+, Fe^{2+}, O_2 and water compounding the pre-irradiated solution. These concentrations were chosen because they are the standard concentrations for the Fricke dosimeter (from 0.1 to 0.001 M for $Fe_2SO_4 \cdot 7H_2O$) in which the oxidation of ferrous ions takes place in an acid medium (H_2SO_4, 0.4 M, this concentration is equivalent to biological tissue). The concentration of oxygen is based on its solubility in water (O'Donnell and Sangster, 1970). The last column of Table 1 shows the initial concentration values we used.

2.3. The mathematical model for reaction kinetics

The model that describes the kinetics in a closed domain of the reaction mechanism is comprised of several nonlinear ordinary differential equations (ODE) forming a system, that is, all of the equations have to be solved simultaneously (Shampine, 1994). One differential equation consists of a mass balance for a single specie, which predicts the expected change in the molar concentration of the species over time. To do this, all the reaction rates leading to production (source term) and to destruction (sink terms) of the given species must be considered. In choosing the species to be included in the overall mass balance for simulation purposes, two criteria were considered. (a) The species must react with at least one of the other species, and such a reaction, whatever its rate, must lead to production or consumption of a certain species. (b) The species concentration is monitored as the experiment progresses as with Fe^{3+}, which was measured at different irradiation doses for each temperature. According to these criteria, only the species HO^- does not need to be considered in the simulations. Therefore, for the other 10 species involved in the reaction mechanism, we included a differential equation of the general form:

$$\frac{d\chi_i(t)}{dt} = f_i + \sum_n \sum_m k^{(i)}_{n,m}\chi_n(t)\chi_m(t) - \chi_i(t)\sum_j k^{(i)}_{i,j}\chi_j(t), \tag{1}$$