

Target Theory Applied in the Radiation Damage Analysis for Organic Detectors.

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Abstract

The Target Theory was used to explain the radiation damage in samples containing 1% (g/L) of 2,5-diphenil-oxazolyl (PPO) diluted in toluene and irradiated with ^{60}Co (1.8 Gy/s). The survival molecules of irradiated PPO following the bi-exponential mathematical model $[0.743 \times \exp(-D/104.3) + 0.257 \times \exp(-D/800)]$. It indicates that a fraction 0.743 of the molecules decay with $D_{37}=104.3$ kGy and 0.257 decay with $D_{37}=800$ kGy. From the Target Theory it was inferred the energies involved in the irradiation damages, which were 0.0363 ± 0.004 eV ($G=3.63 \pm 0.402$ damages/100eV) and 0.0959 ± 0.0492 eV ($G=9.59 \pm 4.92$ damages/100eV). The diameter of PPO molecule estimated from the Target Theory was in the interval of 45.5 to 64.9 Å.

1. INTRODUCTION

In the origins of Radiobiology it was observed that there is a direct relationship between the radioactive dose and the number of microorganisms died by the radiation exposure. In order to express that relationship in mathematical terms, the Target Theory was proposed firstly by Crowther [1]. However, this theory is usually associated to Lea, who improved and consolidated the Target Theory [1,2].

The Target Theory is a model applicable to explain the radiation effects in function of the dose level. This theory uses two basic concepts: (1st) **the target**, for example, a chemical molecule, a crystalline array or an active structure and, (2nd) **the hit**, defined as an event capable to cause damage in the target.

In the Target Theory physiochemical phenomena, such as ions production, electronic shell excitations and solvated radicals' formation may be produced directly in the target or in its neighborhoods, being responsible for the radiation effect. Usually, the studied system is a population

of cells or an active structure in a detector where the effect is evaluated. The hit effect in the target can produce (i) a chemical transformation (chemical reaction) in the studied molecules or (ii) the inactivation of the chemical structure.

Several authors [3,4,5,6] reported that the light output yield and the transparency of the scintillator detectors decrease when exposed to intense radiation dose. The detector efficiency loss, or in other words, its radiation damage can be explained similarly, as the enzyme or protein inactivation. Therefore, the detector degradation can be studied using the Target Theory. This analytical challenge will be applied to the present work focusing the analysis of the scintillating organic system detector. This knowledge was useful in the development of an industrial tomography system using plastic scintillator as a sensitive position detector applied to large objects imaging [7]. In such case, it was used a strong ^{60}Co radiation source together with the organic scintillator detector. In this case, the theory was used to foresee the radiation damage effect along the time.

2. THE TARGET THEORY

There are four subsets for the Target Theory. They are based (a) the number of targets, m , required to produce the damage in the active structure and (b) the number of hits, n , applied in the same target to produce the damage. Thus, four variants of the Target Theory were described in the literature [1], as shown in Fig 1.

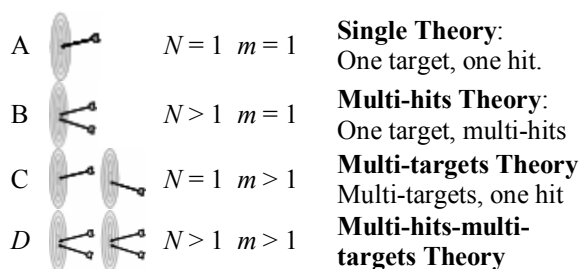


Fig. 1. Different versions for Target Theory

2.1 – The Single Target Theory

Although the literature describes four proposals for the Target Theory (Fig. 1), in practice, the Single Target Theory is the most used.

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The basic principle of this version is that the studied structure has only one target to be damaged and one hit is enough to produce the damage. A graphic interpretation of this idea is shown in Fig. 1A.

In the Single Target Theory the numerical relation between the surviving targets and the dose is foreseen by the exponential relation: $N_s = N_0 \cdot e^{-kD}$, where N_0 is the initial number of targets, N_s is the number of targets not damaged by irradiation and $k=I/D_{37}$ is the damage constant or the target sensitivity to the radiation. When the exponential product $k \times D$ equals one, the exponential term will approximately equal 0.37, or $N_s/N_0 \cong 0.37$, that is, 63% of the irradiated targets were damaged. The dose that causes this effect is called D_{37} or $k \times D_{37} = 1$.

2.2 – Target Volume

One of the applications of the Target Theory is to estimate the molecule (target) volume (V) [1], using the D_{37} and $I(\text{damages}/\text{cm}^3/\text{Gy})$ constants.

$$V(\text{cm}^3) = \frac{I}{D_{37}(\text{Gy}) \times I(\text{damages} / \text{cm}^3 / \text{Gy})} \quad (1)$$

The “ P ” constant represents the damaged active structure quantity per cm^3 and

$$\begin{aligned} I\left(\frac{\text{hits}}{\text{cm}^3 \cdot \text{Gy}}\right) &= \left(\frac{d}{dD}(N_0 \cdot e^{-k \cdot D})\right)_{D=0} \\ &= \frac{N_0 \left(\frac{\text{InitialMolecules}}{\text{cm}^3}\right)}{D_{37}(\text{Gy})} \end{aligned} \quad (2)$$

If the target structure is spherical, its diameter $d(\text{cm})$ can be calculated by the equation:

$$d(\text{cm}) = \sqrt[3]{\frac{6}{\pi} \cdot V(\text{cm}^3)} \quad (3)$$

The hit energy (w) to produce damage in the PPO molecule can be estimated according to:

$$w(\text{J} / \text{mol}) = M(\text{g} / \text{mol}) \times D_{37} \quad (4)$$

or,

$$w(\text{eV} / \text{hit}) = w(\text{J} / \text{mol}) \times 1.036 \times 10^{-5} \quad (5)$$

where the constant represents the ratio:

$$\frac{6.2415 \times 10^{18} (\text{eV} / \text{J})}{6.0225 \times 10^{23} (\text{targets} / \text{mol})}$$

3 – TARGET THEORY APPLIED TO THE ORGANIC SCINTILLATOR

In the organic detector the incident energy of gamma photon is transferred to the detector material producing ionization or excitation and subsequently molecule fragmentations or reactions. Firstly, photoelectric, Compton effects and pair productions generate the primary ions. The ejected electrons can generate secondary ions during their pathways, producing several kinds of free radicals.

Due to the highest ratio of the solvent molecules (toluene, polymer) compared to the scintillator solute molecules (PPO, p-terphenyl, POPOP), it is most likely to occur the radiation interactions in the solvent molecules. On the other hand, the scintillator molecule is the main responsible for the detector performance.

The purpose of this work is to analyze the action of the free radicals in terms of its distance around the scintillator molecule.

4. - METHODOLOGY

The present work constitutes a theoretical interpretation of experimental data, previously described [8]. Basically, samples containing 1% (g/cL) of the scintillator PPO (2,5-difeniloxazol) in toluene were irradiated in different doses in an irradiator of ^{60}Co (Gamma Cell 220 AECL) at a dose rate of 6.46 kGy/h (1.8 kGy/s).

After the irradiation, an aliquot of the radiated solution was evaporated in an oven at a temperature of 40°C and re-diluted in pentane. One milliliter was sampled to determine (GCMS Shimadzu. GCMS-QP5000) the PPO concentration in the irradiated sample, as previously described in the reference [8]. The experimental data of the degradation of the PPO was adjusted by nonlinear regression to a bi-exponential mathematical model. For each exponential component, the D_{37} parameter was estimated.

5. – RESULTS AND DISCUSSION

The experimental evidence is that the PPO degradation obeys a bi-exponential decay model defined experimentally as:

$$[PPO] = 0.743 \cdot e^{-\frac{D}{D_{37}(\#2)}} + 0.257 \cdot e^{-\frac{D}{D_{37}(\#3)}} \quad (6)$$

as shown in Fig.2. Here, D is the dose (kGy), $D_{37(\#2)}=104.3$ kGy and $D_{37(\#3)}=800.0$ kGy

For the ^{60}Co source at dose rate of 6.48 kGy/h it means a linear relationship between dose (kGy) and the time $t(\text{h})$ defined as:

$$D(\text{kGy}) = 6.48xt(\text{h}) \quad (7)$$

Thus, the equation (6) can be rewritten as:

$$[PPO] = 0.743 \cdot e^{-\frac{t(h)}{t_{37}(\#2)}} + 0.257 \cdot e^{-\frac{t(h)}{t_{37}(\#3)}} \quad (8)$$

where $t_{37}(\#2) = 104.3/6.48 = 16.1\text{h}$ and similarly $t_{37}(\#3) = 123.5\text{h}$. Thus, radiation damage can be explained in terms of chemical kinetics as can be inferred from Fig. 2 (top x axis). The mean life time of the irradiated PPO exposed to a radiation flow at a dose of 6.48 kGy/h (1.8 Gy/s) can be estimated as:

$$\bar{T} = \frac{\int_0^{\infty} [0.743 \cdot \exp(-\frac{t(h)}{16.1}) + 0.257 \cdot \exp(-\frac{t(h)}{123.5})] dt}{0.743 + 0.257} \approx 43.7\text{h} \quad (8)$$

On the other hand, if the scintillator system produces an acceptable electronic signal up to 50% of the PPO initial concentration, its working life will be of approximately 16h. In such case, according to the equation (7) the detector can be exposed to 103.7 kGy.

The bi-exponential model does not fit with any theory commonly described in the literature and schematized in Fig. 1. It should be developed a new version of Target Theory or to apply some adoption of the bi-exponential model to some already proposed theories (Fig. 1).

A probable model to explain the bi-exponential scintillator damage is represented in Fig. 3.

Firstly, the radiation excites (first hit) the PPO molecules (PPO pool #1) generating two kinds of PPO molecules (pool #2 and #3). Birks [9] described the excitation process very well. Here it is assumed that the pool #1 represents PPO molecules in its ground state. Pool #2 represents PPO in an excited state and chemically unstable. It represents 0.743 ± 0.046 of the initially excited PPO molecules. It had a half dose $D_{1/2} = 72.3 \pm 9.4$ kGy and $D_{37}(\#2) = 104.3 \pm 13.5$ kGy and its half life at a ^{60}Co source dose rate of 6.48 kGy/h is $T_{1/2} = 11.2 \pm 6.5$ h (Fig. 2). In terms of the Target Theory, pool #2 represents a population from a weak hit occurred in pool #1 which is enough to break it or, in other words, it has a higher cross section.

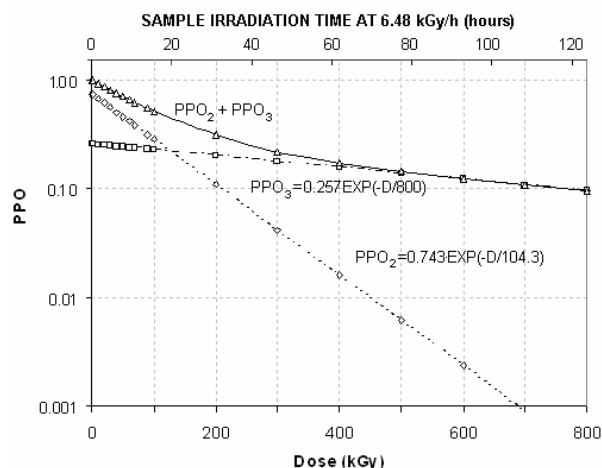


Fig. 2. PPO degradation in function of dose (below axis) and time (above axis).

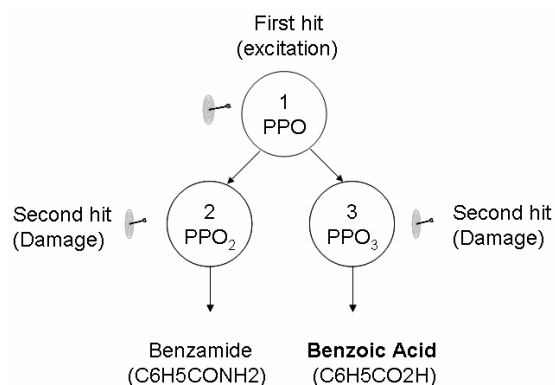


Fig. 3. Compartmental model used to explain the damage in the scintillator.

A third population of excited PPO, represented by the pool #3 in Fig. 3, is more resistant to the radiation, in other words; this population requires a strong hit to cause damage. Its cross section is smaller compared to the excited population #2. It represents 0.257 ± 0.041 of the initially excited PPO molecules. Its half dose $D_{1/2} = 555 \pm 91$ kGy, $D_{37}(\#3) = 800 \pm 131$ kGy and its half life at a ^{60}Co source dose rate of 6.48 kGy/h is $T_{1/2} = 85.6 \pm 14.0$ h (Fig. 2).

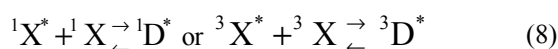
The Target Theory is used to estimate the molecules volume. However, it is not suitable in case where the target is in liquid solution because it will overestimate the true volume. In fact, in such case, the information obtained corresponds to the distance that free radicals are produced, far away from the targets, but capable to affect it by approach mechanisms (for example, Brownian movements).

Table 1 and Fig. 4 show the estimated volumes of PPO molecules according to four different processes. Assuming that the true volume of PPO

can be calculated from its density, then it can be concluded that the volume estimated by the Target Theory presents discrepancies around 40 times. The same comparisons, in terms of its molecular diameter (equation 3) it is 3.4 times larger.

In the toluene, the amount of σ electrons (88%) are larger than the π electrons (12%), thus it is possible that σ electrons have higher probability to be excited.

The excited molecules $1X^{**}$ or $3X^{**}$ combine with neighboring molecules forming dimmers: $1D^{**}$ or $3D^{**}$, according to the following chemical reaction showed in equation (8):



where, superscripts 1, 3 with an * means singlet and triplet excitation states, respectively.

SCINTILLATOR	ESTIMATED VOLUMES	I (hits/cm ³ /Gy) $\times 10^{14}$	VOLUME (cm ³) $\times 10^{-23}$	Φ^* (Å)	w (eV/hit)	G (hits/100eV)
PPO (C ₁₅ H ₁₁ NO) 2.721X10 ¹⁹ molecules/cm ³	Σ Atomic volumes (15C,11H,1N,1O)	-	0.877	2.56	-	-
	Pool # 1 PPO Density (1.06 g/cm ³)	-	34.7	8.72	-	-
	Pool # 2 Target Theory	1.93	4959	45.5	0.0363	3.63
	Pool # 3 Target Theory	0.00874	14301	64.9	0.0963	9.63

* Equations 1 to 3 were used to calculate target volumes and its diameter.

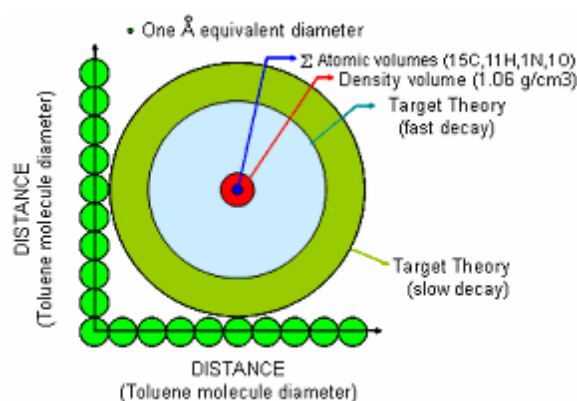


Fig.4 – Geometrical comparison among diameters of the estimated volumes for PPO.

For the toluene, the association constant is $k_a=5.1 \cdot 10^{10} \text{ M}^{-1}\text{s}^{-1}$ and the dissociation constant is $k_d=9.2 \cdot 10^{11} \cdot \text{M}^{-1}\text{s}^{-1}$. Thus, the reaction equilibrium constant for the dimer formation is equal to:

$$K_c (\text{M}^{-1}) = \frac{[{}^1D^*]}{[{}^1X^*] \cdot [{}^1X]} \cong \frac{[{}^3D^*]}{[{}^3X^*] \cdot [{}^3X]} = 0,055 \quad (9)$$

This value is compatible to that expected when the scintillator solution is exposed to radiation, generating excited molecule populations [9] that can have larger sensibility to the reactions with the radiolytic. This value suggests the occurrence of two or more types of targets.

In conclusion, the Target Theory can be useful to explain details of radiation damage and to determine the working time of a detector.

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