Radiation Damage in Scintillator Detector Chemical Compounds. A New Approach using PPO-Toluene Liquid Scintillator Solution as a Model

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Abstract - **The radiation damage effect was evaluated in the PPO-Toluene liquid scintillator solution. Samples containing PPO (1%w/v) diluted in toluene were prepared and irradiated at different doses, using a ^{60}Co irradiator at 6.46kGy.h^{-1}. The radiation effect on the transmittance, light output and chemical modification in the PPO were evaluated before and after irradiation. The loss in transmittance at 360nm decayed exponentially with the dose. The light output decreased as the radiation dose increased. The PPO degraded bi-exponentially with the dose, while the PPO degradation products, such as benzoic acid, benzamide and benzyl alcohol, increased with the dose.**

I. INTRODUCTION

There is a continuous effort to develop detectors capable of resisting high dose radiation in order to survey the environment in nuclear reactors, in particle accelerators, and in industrial irradiation plants. The studies of the phenomena involving the detector damage could be used also as a tool to explain aspects related to the mechanism of the radiation detection [1,2,3,4,14,18].

Organic scintillator has been used in several applications mainly in Nuclear Physics, Astrophysics and particle accelerators research. Despite these detectors are constituted of several chemical elements, the studies evaluating the radiation damage have been emphasized in its overall aspects [5,6,7,8,9,10,11,12,13,15,17,18,19]. This kind of study is appropriated when the resistance to the radiation damage is used to compare the quality among different types of detectors or to evaluate the suitability of their use in rugged environments. Otherwise, this approach is not suitable to infer the causes of the quality loss of the detector. For instance, in the organic detectors the damage can occur due to: (i) the disarrangement in the polymeric chain matrix (e.g.

polystyrene) or (ii) the break or degradation of the scintillator component (e.g. PPO). Furthermore, the organic detector degradation is a complex subject, which needs studies including the heart of the detecting system, that is, its basic components and their interactions.

Few studies detailing the radiation damage in each of the detector chemical constituents have been described, although this knowledge is valuable to develop and to design detectors capable to resist high radiation doses and to understand the origin of the damage mechanism. For example, one scintillator can produce a good physical response in its radiation interaction, however it can be unstable from the energetic point of view, reducing the mean life of the detector. When the radiation resistance is required, the knowledge of the breakdown energy is important as a guidance to select among scintillator options.

Several authors [1,3,4,16] have described that in detectors submitted to strong radiation field, the light yield -conversion and transparency decrease. The loss of these properties is affected differently for several factors, such as the absorbed dose intensity, dose rate, temperature and environmental gas composition during the irradiation.

Pla-Dalmau and col. [7] carried out several studies of radiation damages using different dose rates and pressure conditions. They described that the understanding of the complete mechanisms on the polymeric chain degradation is necessary in order to develop new techniques for detectors construction, capable to increase the stability of the materials when submitted to strong irradiation.

A theory known as "target theory" is an interpretative model to explain the cell killing by radiation. This model has been extended to other fields of interest, especially for bioactive molecules and for chemical reactions [17].

It is known that the target theory is not applicable under water irradiation conditions and this is a major limitation of the method. In liquid solutions, the so-called indirect effects can occur. For example, irradiation of water results in the formation of H$^+$, OH$^-$, peroxide, and other radiolytic products, which, in the liquid state, can diffuse at appreciable distances before reacting. Thus, the

inactivation can occur by the direct action of radiation and by secondary chemical inactivation induced by the free radicals.

Kempner and Schlegel [17] used the target theory to determine the molecular weight of enzymes. Empirically, enzymes are more sensitive to radiation at least two orders of magnitude in liquid solution than in dry state. So far this subject has been studied in dry state, where direct action of radiation occurs on matter and damage is caused entirely by primary ionization.

The present paper evaluates the radiation damage effects in the organic detector, accomplishing the target theory with the compartment method. The damage effects for the liquid solution was isolated in: (a) the scintillator PPO and (b) the toluene. The damage caused by the radiation was evaluated by following measurements: (a) light-output yield (pulse height analysis), (b) optical transmission and (c) analysis of the chemical modifications in the detector. For the analysis of these parameters, a predictable mathematical model, based on compartment theory, was designed to predict the degradation of PPO. A sigmoid model: $Transmi \tan ce = A_2 + (A_1 - A_2)/[1 + (D/D_0)^p]$ was applied to predict the transmittance in function of the dose D.

II. MATERIAL AND METHODS

Twenty samples were irradiated in duplicated containing toluene and PPO. Twenty more samples in duplicate containing only the toluene were irradiated in a Gammacell type irradiator containing ^{60}Co source of 334 TBq (9021 Ci), at a dose rate of 6.48 kGy h^{-1}. The doses were extended up to 1000 kGy, to accentuate the production of the damages and for better definition of the concentration curves for the resulting formed chemical products. After the irradiation, the toluene contained in the flasks was evaporated in an oven at 40 ^{o}C. Subsequently, no irradiated toluene (10 mL) was added, in order to restore the sample. A small source of ^{137}Cs was used to study the light yield of the irradiated samples. The source was fixed in the bottom of the flask (external face) and placed in the measurement chamber of the Liquid Scintillator Beckman model LS150. This procedure was repeated for each sample. The signal generated from the two-phototubes processed by the coincident and sum circuit was connected to an amplifier (Ortec mod. 450). The output signal from this amplifier was connected to a multichannel analyzer ADCAM (Ortec mod. 918) and, simultaneously, to an oscilloscope (Tektronix mod. TDS 410A 100 MHz). From these measurements, the spectra of the source ^{137}Cs and the signal pulse shape from the oscilloscope screen were inferred for pulse height analysis. An aliquot of 1 μL from each sample was taken for mass spectrometry analysis (Shimadzu mod. GCMS-

QP5000) and 1 mL was used to know the transmittance (Shimadzu spectrophotometer mod. UV-1601 PC).

Fig. 1 displays the outline of the compartmental model adopted to explain the degradation of PPO in the liquid scintillator. This model is represented mathematically by the system of differential equations:

$$\frac{df1}{dD} = -(k1,3 + k1,4) \cdot f1 \qquad f1(0) = I1$$

$$\frac{df2}{dD} = -(k2,3 + k2,4) \cdot f2 \qquad f2(0) = I2$$

$$\frac{df3}{dD} = k1,3 \cdot f1 + k1,4 \cdot f2 - k3,0 \cdot f3 \qquad f3(0) = I3$$

$$\frac{df4}{dD} = k1,4 \cdot f1 + k2,4 \cdot f2 - k4,5 \cdot f4 \qquad f4(0) = I4$$

$$\frac{df5}{dD} = k4,5 \cdot f4 \qquad f5(0) = I5$$

where:

f1 ≡ concentration of PPO degraded by secondary processes of damages (i.e. reactions with free radicals produced in the irradiated solution),

f2 ≡ concentration of PPO degraded by the primary process of radiation (γ photons hitting PPO directly),

f3 ≡ concentration of benzamide produced by irradiation,

f4 ≡ concentration of benzoic acid produced by irradiation,

f5 ≡ concentration of benzyl alcohol,

$f_i(0)=I_i$ is the initial value for the i-compartment function and $k_{i,j}$ = fractional probability of conversion (kGy-1).

The AnaComp [19] software was used to estimate the unknown parameters of the model showed in Fig. 1.
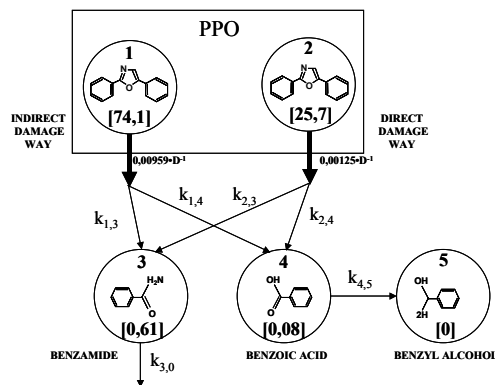

Figure 1-Compartmental model used to explain the degradation of PPO (2,5-Dipheniloxazole) and its radiation damage products. The values between brackets, [], represent the initial concentrations (%), determined experimentally in the non- irradiated sample. The compartments represent, respectively: (1) the PPO destroyed indirectly or secondarily by actions of radiolytic in toluene, (2) the PPO damaged directly or primarily by the radiation, (3) benzamide, (4) benzoic acid, (5) benzyl alcohol and (0) other compounds not identified. The constant ki,j represents the fractional probability of conversion (kGy-1).

According to the target theory, the **w** and **G** parameters were calculated, i.e., *w(J/mol)=MM(g/mol)/k$_{i,j}$(Gy^{-1})* and *w(eV/hit)=w*(J/mol)×1.036×10^{-5}, were *MM* is the target

molecular mass; $k_{i,j}(kGy^{-1})$ is already defined and showed in Table 1. The factor 1.036×10^{-5} is the ratio

$$\frac{\text{joule} \rightarrow \text{eV conversor Factor}}{\text{Avogadro number}} = \frac{6.2415 \times 10^{18}(eV/J)}{6.0225 \times 10^{23}(T\arg et/mol)}$$

The radiation chemical yield, **G** value, was calculated as **$G(hit/100eV)=100/w(eV/hit)$** and **$G(mol/J)=1/w(J/mol)$**.

III. RESULTS AND DISCUSSION

The photopeaks of the liquid scintillator using irradiated PPO, excited under a ^{137}Cs source, as a function of the dose are shown in Fig. 2.
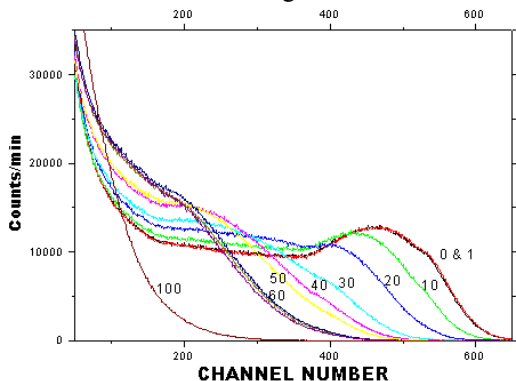

Figure 2-^{137}Cs Spectra. Liquid scintillator contained 1% (w/v) of PPO (2,5-Dipheniloxazole). Numbers beside each curve represent the respective dose (kGy).

The loss of the energetic resolution after 40kGy was so intense that the photopeaks could not be observed because they merged in the Compton area. Then, this kind of analysis was useful until the value of 40kGy. On the other hand, results using Fig. 3 are another way to improve this analysis.
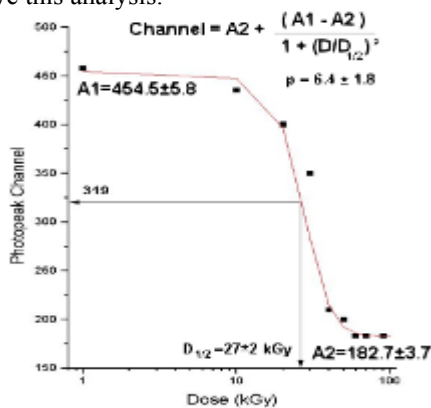

Figure 3 – Light output yield based on the photopeak position. A_1 and A_2 are the upper and lower asymptotic parameters respectively, $D_{1/2}$ is a balance value while p is an exponential parameter associated with curve slope.

As observed in Fig. 3, the displacement of the photopeak fits to a sigmoid curve, i.e., it presents a plateau for doses in the range from 0 to 10 kGy, followed by a fast

slope in the range from 10 to 40 kGy and a bottom plateau after 60 kGy. It was concluded from the $D_{1/2}$ parameter that a dose of approximately 27kGy is required to decrease by half the detector performance.

The pulse height analysis from the shape of signals measured directly by an oscilloscope is shown in Fig. 4. As it can be inferred, the behavior of the pulse height with the dose showed a complex function. In fact, Fig. 4 supplied similar information already described in the analysis of figures 2 and 3. However, these results generated a curve profile with a sequence of plateaus and slopes and it was not susceptible to be treated with a mathematical model.
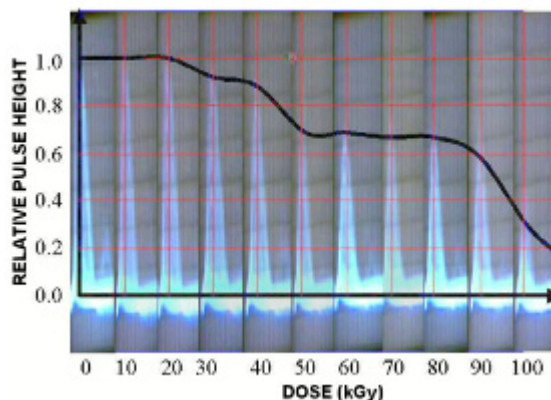

Figure 4- Pulse height analysis in function of the dose. Source: ^{137}Cs. Pulses measured by 100MHz oscilloscope.

The transmittance curves as a function of dose in the range from 320 to 800nm are exhibited in Figure 5.
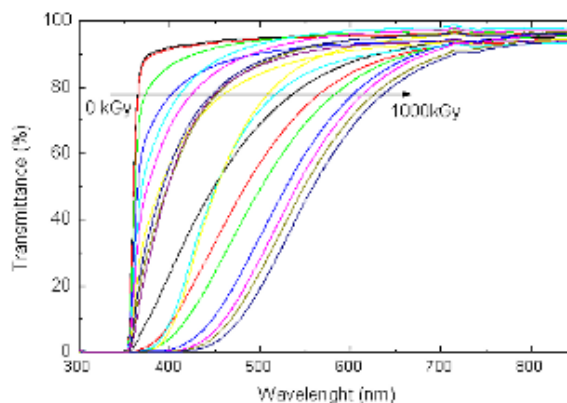
Figure 5 – Transmittance of the samples irradiated with different doses. Samples were irradiated containing 1% of PPO in 10 mL of Toluene. Irradiated Toluene was evaporated and re-suspended with no irradiated toluene.

As it can be observed the transmittance decreased in function of the dose. Considering that the PPO fluorescence peak occurs at 360nm the transparency was evaluated in that value, as shown in Fig. 6. The transmittance decreased exponentially with the dose showing a strong correlation (r=0.9989).

The transparency loss and the light yield decreased, i.e. the degradation of the characteristics of the detector should be associated to the chemical changes occurred inthe scintillator that degrades it in other chemical components. As shown in Table 1 and 2, at least three other products: benzyl alcohol, benzoic acid and benzamide were generated in irradiated PPO-toluene solution. These substances can generate color and/or chemical quencher and they should be responsible for the transmittance loss.
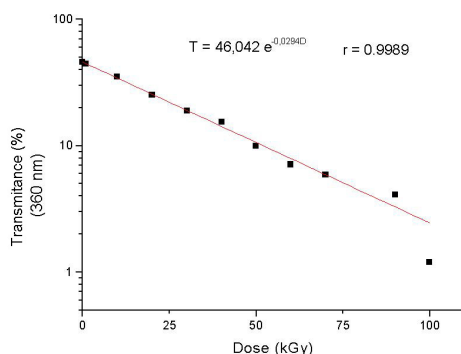

$T = 46,042 \, e^{0.0294D}$ $r = 0.9989$

Figure 6 – Transmittance at 360 nm for irradiated samples and reconstituted with no irradiated toluene.

Table 1 – Non-linear least square parameters, molecular mass and quantities determined with gas chromatograph-mass spectrometer.

PARAMETER	$(\times 10^{-6})$	VALUE ± ERROR
K1,1 (Gy^{-1})	9.590	± 1.240
K1,3 (Gy^{-1})	4.210	± 1.400
K1,4 (Gy^{-1})	5.380	± 1.870
K2,2 (Gy^{-1})	1.250	± 0.205
K2,3 (Gy^{-1})	1.700	± 0.680
K2,4 (Gy^{-1})	0.453	± 0.710
K4,5 (Gy^{-1})	0.100	± 0.148
K3,0 (Gy^{-1})	1.160	± 0.791
INITIAL CONDITIONS	CONTENT	
	(%)	(g)
I 1 PPO$^\bullet$ ($C_{15}H_{11}NO$) Molec. Mass: **221.26** g/mol	74.3 ± 4.57	0.0743
I 2	25.7 ± 4.13	0.0257
I 3 Benzamide ($C_6H_5CONH_2$) Molec. Mass: **121.14** g/mol	0.61§	0.00061
I 4 Benzoic Acid($C_6H_5CO_2H$) Molec. Mass: **122.12** g/mol	0.08§	0.00008
I 5 Benzyl Alcohol (C_7H_8O) Molec. Mass: **108.14** g/mol	0.0§	0.0

Fig. 7 displays the behavior of the PPO scintillator and its degradation products in function of the dose. As it can be inferred, the same concentration of PPO, benzoic acid and benzamide was found around 200kGy. The curves showed that PPO degraded fitting a bi-exponential function with the subsequent growth of the benzoic acid and benzamide (Table 1 and Fig. 7).

Two-damage processes can explain the bi-exponential degradation behavior of irradiated PPO and therefore the curve was split into two exponentials.

Table 2 – Concentrations of chemical compounds measured and calculated values (* AnaComp software [19]).

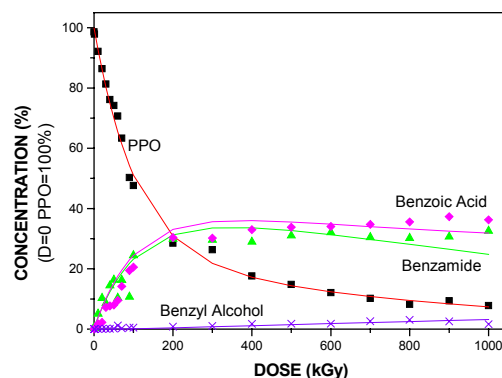|	CONCENTRATION (%)							
DOSE	PPO (2,5-Dipheniloxazole)		BENZAMIDE		BENZOIC ACID		BENZYL ALCOHOL	
(kGy)	Observ	Calc*	Observ	Calc*	Observ	Calc*	Observ	Calc*
0	98.61	99.80	0.61	0.61	0.08	0.08	0.00	0.00
1	97.88	99.06	0.25	0.96	0.10	0.47	0.06	0.00
10	92.10	92.70	5.07	3.99	1.76	3.77	0.08	0.00
20	86.38	86.23	10.25	7.06	2.24	7.10	0.09	0.01
30	81.33	80.33	8.54	9.83	7.18	10.12	0.10	0.02
40	76.10	74.94	14.43	12.35	7.69	12.85	0.13	0.03
50	74.19	70.02	16.31	14.63	7.97	15.32	0.20	0.04
60	70.69	65.52	10.33	16.70	9.47	17.55	1.17	0.06
70	63.36	61.42	16.28	18.57	14.17	19.56	0.25	0.08
90	50.30	54.22	10.70	21.79	19.46	23.02	0.52	0.12
100	47.60	51.08	24.44	23.17	20.55	24.50	0.51	0.14
200	28.53	30.90	29.89	31.23	30.38	33.07	0.80	0.44
300	26.32	21.84	29.54	33.58	30.16	35.64	1.08	0.78
400	17.62	17.19	28.96	33.61	32.99	35.98	1.76	1.14
500	14.79	14.37	30.97	32.67	33.81	35.51	1.79	1.50
600	12.13	12.37	32.06	31.31	34.05	34.78	1.82	1.85
700	10.18	10.80	30.45	29.76	34.75	34.01	2.65	2.19
800	8.25	9.49	30.20	28.13	35.57	33.25	3.09	2.53
900	9.39	8.36	30.64	26.48	37.32	32.53	2.58	2.86
1000	7.83	7.37	32.54	24.83	36.24	31.85	1.65	3.18

Figure 7 – Concentration of PPO (2,5-dipheniloxazole) and of its degradation products in function of dose. The continuous curves were generated by AnaComp program[19], using the model described in Fig. 1.

The fast slope ($74.1 \bullet e^{-0.00959 \bullet D}$) can be explained as indirect damage. Firstly, the gamma photons interact with the molecules of toluene, which generate radiolytic sub-products. Subsequently, PPO reacts with these radicals. Gases dissolved in the solution, like O_2, can contribute to the enhancement of the radiolytic products. On the other hand, the slow slope ($25.7 \bullet e^{-0.00125 \bullet D}$) can be interpreted as the damage caused by primary radiation interaction with

targets, i.e., direct hitting of γ-photons to PPO. As the dose increases, the amount of radiolytic products tends to saturation or reach equilibrium. Thus, high gamma fluxes mean high absorbed dose, which increase the probability of the gamma photon hits directly the PPO molecule. Above 97.7kGy the primary damage in the PPO at 1% (mass/vol in toluene) becomes predominant.

IV. CONCLUSION

The damage of the radiation on the liquid scintillating system (PPO + toluene) showed that the main damage occurs in PPO, since the samples irradiated without PPO did not generate the products benzamide, benzoic acid and benzyl alcohol. The liquid scintillating system is reasonably very sensitive to the radiation due to the damage on the scintillator PPO. The pulse height analysis showed that doses from 30 to 40 kGy generated a substantial loss of quality of the sensor (liquid scintillating) and it was half reduced at 27 kGy. The transparency of the solution for photons produced in the liquid scintillating decreased as a mono-exponential function. The compartmental model analysis considering five components (PPO, benzamide, benzoic acid and benzyl alcohol) was satisfactory as a predictive model to estimate the products in function of the dose. The coefficient $r^2 = 0.985636$ assures that the model was capable to explain 98.6% of the experimental variations among the experimental points of concentration.

V. ACKNOWLEDGMENT

VI. REFERENCES

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