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Comparison of alanine dosimeters using silicone as their binder to a commercial, polystyrene-bound, alanine dosimeter

S. GALINDO* AND F. UREÑA-NÚÑEZ
Instituto Nacional de Investigaciones Nucleares
Apartado postal 18-1027, Col. Escandón, C.P. 11801, México D.F., Mexico

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ABSTRACT. The feasibility of practical boron-containing alanine ESR dosimeters for gamma-neutron mixed field irradiation dosimeters depends in part on whether the γ response characteristics of these silicone-bound dosimeters are comparable to those of a commercially available dosimeter that has been used by the International Atomic Energy Agency (International Dose Assurance Service) as a transfer reference dosimeter. This work presents the results of the comparison of 3 batches of silicone-bound alanine dosimeters. The first batch consists of a mixture of alanine and boric acid; the second, alanine and borax; and the last contains only alanine. Results indicate that γ response characteristics of the silicone-bound samples are comparable to those of the commercial, polystyrene-bound, alanine dosimeter and that silicone has a strong potential as a binding substance for alanine ESR dosimetry.

RESUMEN. La viabilidad de dosímetros prácticos de REE (resonancia de espín electrónico) que contengan boro, para su uso en campos de irradiación mixtos de neutrones y gammas, depende en parte en si las características de su respuesta a gammas de estos dosímetros aglutinados con silicón, son comparables a aquellas de un dosímetro comercial el cual ha sido ya utilizado por la Agencia Internacional de Energía Atómica (Servicio Internacional de Aseguramiento de Dosis) como un dosímetro de referencia para intercomparación. Este trabajo presenta los resultados de la comparación de 3 grupos de dosímetros de alanina aglutinados con silicón. El primer grupo consiste en una mezcla de alanina y acido bórico; el segundo, alanina y borax; y el último sólo contiene alanina. Los resultados indican que las características de respuesta a las gammas de las muestras aglutinadas con silicón son comparables a las del dosímetro comercial de alanina aglutinado con poliestireno y que el silicón tiene un fuerte potencial como aglutinante en la dosimetría de alanina por REE.

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1. INTRODUCTION

Studies for the development of an alanine ESR-dosimeter for gamma and thermal neutron mixed field irradiation are carried out at Instituto Nacional de Investigaciones Nucleares

*Corresponding author. Fax: [+52] (5) 521 9408, electronic mail: sgu@nuclear.inin.mx

(ININ) México. The initial studies consisted in increasing the alanine ESR signal response to thermal neutrons by mixing boron compounds to alanine. It has been shown that the addition of boron compounds, such as borax and boric acid, to alanine dosimeters, enhance their response to thermal neutrons [1]. This opens the possibility of establishing an ESR thermal neutron fluency measurement technique based on the ESR signal enhancement of alanine due to the addition of boron to the samples [2]. Furthermore, the ESR-alanine-silicone system has proven to be useful for measuring dose distributions in electron irradiation [3]. This fact, together with the perspective of the boron-containing alanine-silicone system use in neutron dose evaluations, leads to a further possibility of its application in mixed radiation fields. For the latter application it becomes necessary to subtract, from the ESR signal of an hypothetical dosimeter irradiated in a mixed γ-thermal neutron field, the gamma dose contribution to the signal, so the remanant intensity can be attributable to the thermal neutrons. This proposed technique will enable us to identify the γ-dose contribution in a mixed γ-thermal neutron irradiation field. Therefore γ dose contributions have to be accurately and correctly evaluated if we wish the technique to be reliable. Such accuracy requirements depend on whether the γ response characteristics of these boron containing dosimeters are comparable to those of an accepted transfer reference dosimeter.

Therefore, it was thought convenient to compare the boron containing silicone-bound dosimeters to that employed by the International Atomic Energy Agency (International Dose Assurance Service) as a transfer reference dosimeter [4–6]. The latter dosimeter uses polystyrene (PS) as binder and it is currently handled by Hitachi Cable Ltd., under the retail name of AMINOGRAY$^{\text{TM}}$. The excellent response characteristics of the polystyrene-bound AMINOGRAY$^{\text{TM}}$ are reported elsewhere [4, 5].

Polystyrene and paraffin are the typical binding substances used in the preparation of alanine dosimeters [7]. However, the foreseen advantages of silicone as a binder substance are numerous. Normally commercial room-temperature vulcanizing (RTV) silicone contains no significant paramagnetic species and under irradiation no observable radicals are produced. Also, silicone rubbers are exceptionally resistant to decomposition by heat, differing in that aspect from the extensively used paraffin binder.

Additionally, silicone is also water repellent. But, possibly the prime advantage on the use of silicone over paraffin and polystyrene is that silicone can be molded at room temperature, so other chemical substances (borax, boric acid) besides alanine, can readily be incorporated to the pellets.

This work reports experimental data on the comparison of 3 batches of silicone-bound alanine dosimeters. The first batch consists of a mixture of alanine and boric acid; the second, alanine and borax; and the last contains only alanine. Finally, as mentioned, measurements on AMINOGRAY$^{\text{TM}}$, the chosen comparison standard, are included.

The following sections describe the preparation methods and physical features of the dosimeters, made at laboratory-scale by ININ, México [8]. Then, the irradiation conditions and a comparison of the experimental responses are mentioned. Finally, the results of the comparison are pondered.

2. EXPERIMENTAL

2.1. THE DOSIMETERS

The dosimeters use room-temperature-vulcanizing (RTV) silicone as the binder. The RTV silicone elastometer used in this work is supplied as a one-component uncured paste-like rubber by Dow Corning™ de Mexico, S.A. de C.V. (Prod. No. 24326). Dosimeters are prepared as follows.

2.1.1. Alanine-silicone

DL-α-[CH_3-$CH(NH_2)$-COOH] alanine powder, as supplied by the manufacturer (Merck, 99%) in form of polycrystalline powder, is finely ground in a mortar and homogeneously mixed into the RTV silicone gel. No annealing to erase predose signals of the powder is performed, nor are the grains sieved. The ratio of silicone: alanine is 1 g of alanine per milliliter of silicone. This insures a uniform mix of good consistency.

The mixture is then placed into a plastic syringe which is used in turn to introduce the mixture into open-ended cylindrical molds. The remaining excess of mixture that protrudes from both open ends is removed by leveling the ends with a straight edge spatula. After 24 hours, vulcanization has taken place and the batch is ready for extraction from the molds. This is done by pressing the pellets from one of the two open ends of the mold with a blunt object such as a rod of the same diameter as the mold.

The molds were manufactured by drilling a set of holes (3.5 mm diameter) through a nylamid block (27.2 mm thick).

2.1.2. Alanine-boric acid

DL-α-alanine powder (Merck 99%) and boric acid powder (H_3BO_3) (Baker 99.8%) 1:1.5 stoichiometric proportion are dissolved together in water. The solution is stirred thoroughly and is gently heated to induce evaporation. The mixture, once dried, forms lumps that are ground in a mortar and passed through a sieve (No. Mont-Inox ϕ= 0.0625 mm) to obtain a fine powder.

The powder mixture is blended with the silicone gel in a proportion of one gram of mixture per milliliter of binder. The procedure for making the pellets is the same as the one described above.

It must be mentioned that, when alanine and boric acid are mixed together in a solution they may experience a chemical reaction commonly known as a "Lewis reaction." As a result of this reaction a fraction of alanine and the acid react to form alaninehydroboride. But since a low fraction of boric acid, when added to water, dissociates into free hydrogen ions, the reactivity of alanine-boric acid can be significant. The extent of the above mentioned reaction has been already investigated using ESR and potentiometric titration methods [1]. Titration measurements reveal that the amount of alanine remaining in the mixture is about $54 \pm 5\%$ of the nominal amount.

The mixture has also been analyzed by x-ray diffraction and NMR spectroscopy. Diffractograms show that the mixture is composed of α-alanine, boric acid and, a component or components producing an extra set of unidentified lines, presumably of alaninehydroboride. For this chemical compound it was not possible to find information in currently used data banks, both for x-ray diffraction and NMR analysis.

2.1.3. Alanine-borax

DL-α-alanine powder (Merck 99%) and borax ($Na_2B_4O_7.10H_2O$) (Baker 101.5%) were dissolved in water in a 1:1 stoichiometric proportion. The method for preparing the mixture and obtaining the pellets is exactly the same as those described above.

2.2. COMPARISON STANDARD

AMINOGRAY^{TM} was chosen as the comparison standard in this study, for its excellent characteristics as a transfer reference dosimeter [5]. This dosimeter was used as supplied directly by the manufacturer.

2.3. PHYSICAL CHARACTERISTICS

The dimensions and density of each dosimeter were examined using a digital caliper (Mitutoyo "Digimatic" CD-15) and an analytical balance (Sartorius "Research"), and average density of ten AMINOGRAY^{TM} dosimeters is 2.98 ± 0.01 mm, 30.40 ± 0.16 mm and 1.227 ± 0.014 g/cm^3, respectively. While for 30 samples of alanine-silicone pellets the average diameter, average length were of 3.60 ± 0.03 mm and 27.29 ± 0.10 mm respectively. The measured average densities for the alanine-silicone, alanine-borax and alanine-boric acid were: 1.079 ± 0.021 g/cm^3, 1.117 ± 0.035 g/cm^3 and 1.121 ± 0.038 g/cm^3, respectively.

2.4. IRRADIATION CONDITIONS

Irradiation was performed using a ^{60}Co gamma-ray source (Gamma Cell AECL 220). The dose rate was of 0.6 kGy/h. Dosimeters were irradiated in sets of twelve. Each set was formed by drawing three dosimeters out from each one of the four batches of dosimeters, *i.e.*, alanine-borax, alanine-boric acid etc. Each set was irradiated collectively to doses of 1, 5, 10, and 30 kGy at a temperature of 25 ± 3°C, between two polystyrene walls of thickness 4 mm so as to establish electron equilibrium. A fifth set was not irradiated, to measure the zero-dose signal response.

2.5. ESR MEASUREMENTS

The ESR readings were made immediately after irradiations, and the dosimeters were stored at room temperature. The ESR measurements were done with a Varian E-15 ESR Spectrometer operating at x-band microwave frequencies, with the following operational settings: The microwave power was 1 mW. Those for power saturation studies were of 0.1 to 8 mW; the field modulation amplitude at 100 kHz for zero-dose and dose response evaluations was 0.4 mT; for modulation-broadening appraisals the amplitude ranged from 0.1 to 1.0 mT; the magnetic field was set around 330 mT and the scan range, about the central field, was a 20 mT linear sweep in 4 min. Measurements were performed at room temperature. The dosimeter was positioned in the cavity by means

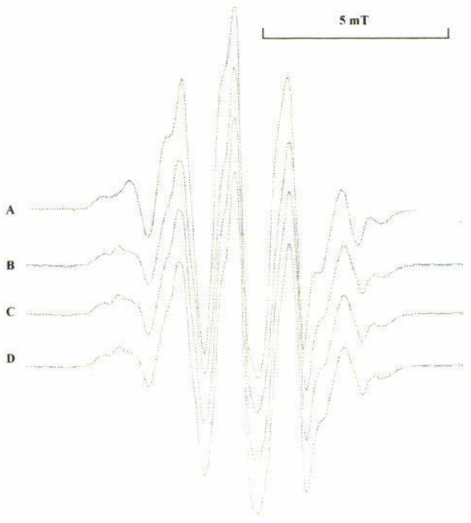

FIGURE 1. First derivative of the ESR spectra of gamma-ray irradiated samples (1 kGy) of (A) AMINOGRAY™, (B) silicone-bound alanine, (C) silicone-bound alanine-boric acid, and (D) silicone-bound alanine-borax. Microwave power 4 mW; modulation amplitude 0.4 mT (100 kHz); time constant 0.3 s.

of a fused-quartz sample tube holder (inner diameter = 3.7 ± 0.01 mm, wall thickness 0.4 ± 0.01 mm). Fading characteristics were not appraised in this experiment as they are reported elsewhere [8, 9].

3. RESULTS AND DISCUSSION

Figure 1 shows the first-derivative ESR spectra of the four kinds of alanine dosimeters irradiated to 1 kGy. Spectrum "A" of Fig. 1 corresponds to that of the AMINOGRAY™ dosimeter. Spectrum "B" is the alanine silicone-bound signal, while "C" and "D" are the alanine-boric acid and the alanine-borax spectra, respectively. The spectra for the three types of silicone bound dosimeters are very similar to that of the pure alanine, as is the spectrum for the AMINOGRAY™ dosimeter. However the latter shows a slightly different shape at the central peakand at the extremes. The two types of the shape, on one hand that for "B", "C", and "D" and on the other, that for "A" can be observed from the same alanine sample at different power levels [10]. But the interesting point here is that all the samples in Fig 1 were subjected to the same microwave power level. A possible explanation to the shape difference is that the cavity's Q factor, might be different for AMINOGRAY™ causing a different power level on the sample and thus, this slight difference in its shape. In addition this indicates that the Q factor for the cavity, when the samples "B", "C", and "D" are measured, does not vary.

Characteristics of the radiation induced peak-to-peak signal intensity, dose response, were examined as function of the dose in the 1 to 30 kGy range. The dotted line in Fig. 2 shows the dose response curve for γ-irradiated silicone-bound dosimeters for this

TABLE I. Relative ESR signal intensity response of the alanine dosimeters at 1 kGy (AMINOGRAY™ = 100%)

AMINOGRAY™	BORAX-SILICONE	BORIC ACID-SILICONE	ALANINE-SILICONE
100%	13.5%	32.2%	67%

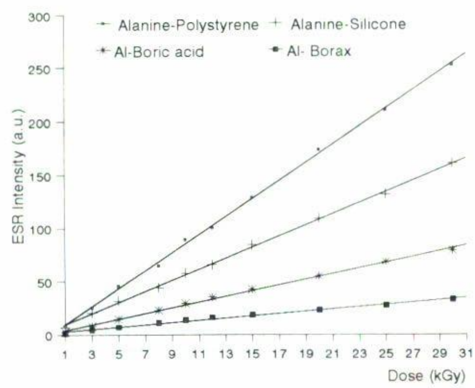

FIGURE 2. Dose response curves for alanine dosimeters gamma-ray irradiated in the 1 to 30 kGy range.

dose range. Also shown in the same figure is the dose response curve for AMINOGRAY™ (solid line). The linear regression correlation coefficients for AMINOGRAY™ and the silicone-bound dosimeter are 0.9995 and 0.9992, respectively, showing a relatively good linear response. Similar correlation coefficients were obtained for the two types of boron containing alanine-silicone dosimeters (borax = 0.9991, boric acid =0.9992).

A comparison of the relative signal intensity response of all four types of dosimeters was made at 1 kGy (Table I).

Dose response depends essentially on the amount of alanine that the pellets contain and on their microwave cavity filling factor. This factor depends on the sample's dielectric constant and, hence, on the composition of the sample. The influence of the dielectric constant is especially significant in the case of wide samples. The volume of the three silicone-bound dosimeters is the same, but their composition is not, and therefore their filling factor might not be the same for the three. Hence their signal response might not depend exclusively on their alanine content. However, an examination of the experimental data answers this question. For example, the molecular weights of alanine and borax are 89.09 and 381.24 respectively, such that the expected response ratio of alanine-silicone to alanine-borax (1:1 stoichiometric proportion) silicone-bound dosimeters is $(89.09/381.24) \approx 0.23$. This value is consistent with the measured value

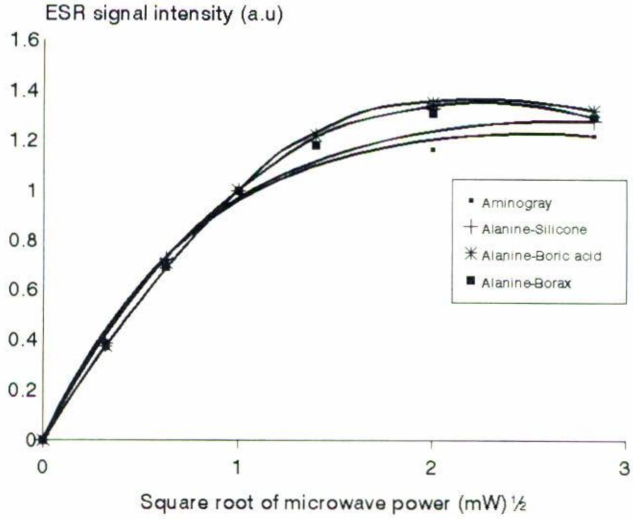

FIGURE 3. Signal amplitude response as a function of the square root of the powder for the four types of irradiated dosimeters (1 kGy).

13.5%/67% ≈ 0.2 given in Table I. For the boric acid, the quantity of alanine by weight in the dosimeters, as stated previously, is 46 ± 5% lower than that in the dosimeters containing exclusively alanine. As consequence, their signal intensity should be smaller than that of alanine-silicone dosimeters of the same percentage. An examination of Table I for this case gives a value of 32.2%/67% ≈ 0.48. This is in fair agreement with the value quoted above. Therefore the proportional signal response for the silicone-bound dosimeters depends only on their proportional alanine content.

The zero-dose response was investigated for the four types of dosimeters. The measured apparent values for unirradiated AMINOGRAY™ and the silicone-bound alanine dosimeter were between 2 and 3 Gy. This is probably due to radicals produced while grinding the powder during the manufacturing process. The observed signals for the unirradiated alanine-boric acid and the alanine-borax specimens were very weak owing perhaps to the fact that the mixtures used in these dosimeters were recrystallized in water during the production stage and to the fact that their alanine content is lower than the other two types of dosimeters. In any case, the zero-dose responses for the latter two types of dosimeters are negligible.

Signal amplitude response for all irradiated specimens as a function of the microwave power level was studied at the following power levels: 0.1, 0.4, 1.0, 4.0, and 8.0 mW. The ESR signal intensities for the four types of dosimeters are plotted in Fig. 3 as function of the square root of the power. The absorbed dose is 1 kGy for all four cases. As expected, the signal intensities show a linear dependence for low microwave power. It is observed that the linear region falls below 1.0 $(\mathrm{mW})^{1/2}$ while saturation is reached around 2.0 $(\mathrm{mW})^{1/2}$ for all samples.

Preliminary studies of the line shape dependence on modulation, for the irradiated silicone-bound dosimeters, show that negligible line broadening occurs for modulation

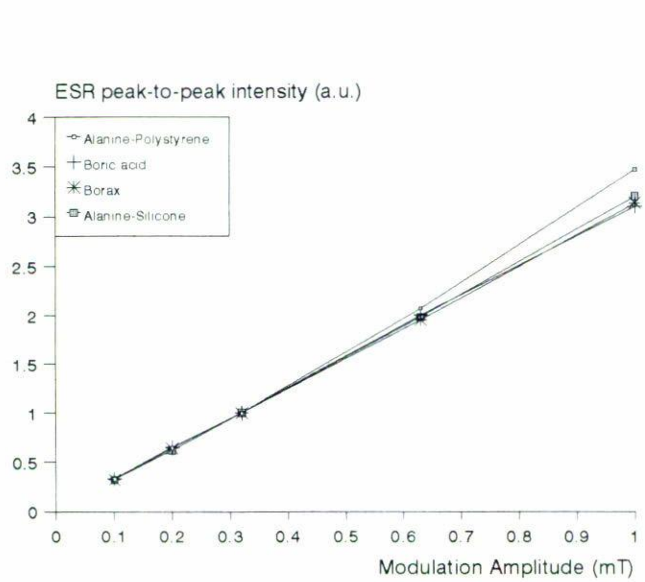

FIGURE 4. Plot of the ESR peak-to-peak intensity as a function of the modulation amplitude for the four types of irradiated dosimeters (1 kGy).

amplitudes smaller than 0.32 mT. In contrast, modulation broadening for irradiated AMINOGRAY^{TM} occurs at larger modulation amplitudes (near 0.63 mT), probably due to its larger intrinsic linewidth. Fig. 4 shows a plot of the ESR peak-to-peak intensity as a function of the modulation amplitude for all four dosimeter types. An approximately linear dependence was observed for all curves for modulation values below 0.32 mT and a slight departure from linearity at 0.63 mT, for AMINOGRAY^{TM}. This small difference in the slopes is not important for dosimetric purposes since dosimetric measurements are performed well below 0.63 mT. However, definite conclusion on this small difference in the slopes will be derived from a further study.

4. CONCLUSIONS

Intercomparison of radiation induced ESR spectra of alanine dosimeters were carried out. The intercomparison was performed among alanine dosimeters using silicone as the binding substance (ININ) and that employed by the International Atomic Energy Agency (International Dose Assurance Service) as a transfer reference dosimeter using polystyrene (AMINOGRAY^{TM}). The main characteristics studied were: zero dose signal, dose response, peak to peak dependence on the modulation amplitude and microwave power. Results from this study are summarized as follows: Signal intensity for the silicone-bound dosimeters depends only on the amount of alanine existing in the sample. Dose response linearity of the silicone-bound alanine dosimeter is acceptable over the dose range 1 to 30 kGy. Dose response of the silicone-bound dosimeters has a lower slope than that of AMINOGRAY^{TM}. Zero-dose apparent response for all the unirradiated dosimeters is relatively low.

The results of this investigation show that RTV silicone has promising potential as a useful binding substance for alanine-ESR dosimetry. The relatively large variation in the physical length dimensions of the pellets observed in this study can be reduced by a more careful pellet production. However length scattering is not critical for practical ESR measuring reproducibility while low scattering in the dosimeter diameter dimension and density are crucial [11]. Low scattering is achieved for the latter two parameters silicone-bound dosimeters. The dose response of the silicone-bound dosimeters can be improved by either increasing the alanine content of the sample or by optimizing the pellet dimensions in order to enhance the filling factor of the microwave cavity so to augment its Q factor. The results here presented show that the boron-containing alanine ESR dosimeters have γ response characteristics comparable to those of an international transfer reference dosimeter. This fact may lead to a future development of feasible practical boron-containing alanine ESR dosimeters for gamma-neutron mixed field irradiation measurements.

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