Effect of Relative Humidity on Dose Response of Effervescent Glycine Pellet Dosimeters

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Abstract
Glycine pellet dosimeter based on spectrophotometric read-out method has a useful dose range of 100 to 1000 Gy and is apt for routine dosimetry in low dose applications of radiation processing. The read-out method requires dissolution of these pellets in acidified solution of ferrous ammonium sulphate and xylenol orange, but due to appreciable hardness of these pellets it is required to stir the solution for complete dissolution which is generally not preferable. Hence fast dissolving pellets were fabricated using sodium bicarbonate as an effervescent agent. As sodium bicarbonate is hygroscopic, study of effect of relative humidity on dose response of these pellets was carried out in the present work.

Keywords: relative humidity; dose response; effervescent glycine
1. INTRODUCTION

Glycine pellet dosimeter based on spectrophotometric read-out method has a useful dose range of 100 to 1000 Gy and is apt for routine dosimetry in low dose applications of radiation processing [1]. Spectrophotometric read-out method is based on indirect oxidation of ferrous ions, when a known amount of irradiated amino acid is dissolved in an aerated aqueous acidic solution containing ferrous ammonium sulphate and xylenol orange. Radiation induced free radicals in amino acid during dissolution in FX solution, form peroxy radicals with oxygen. These radicals subsequently oxidize ferrous ions to ferric ions. Xylenol orange forms a complex with ferric ions. This complex is estimated using a visible spectrophotometer. The change in absorbance is proportional to dose.

Glycine pellets were fabricated by means of dry compaction technique using a manual hydraulic press and 13 mm tungsten carbide die. Binding property of glycine is excellent when compared to other amino acids, hence pellets were fabricated without using any binder. Friability and hardness of these pellets were found to be <0.5% and 16.00 ± 0.62 kg respectively. Due to appreciable hardness, dissolution of each pellet in FX solution requires stirring for at least 3 mins [1]. This aspect of the dosimeter is tedious and time consuming, which might render it less preferable for routine dosimetry. Hence fast dissolving pellets were fabricated using sodium bicarbonate as an effervescent agent which increases the disintegration of pellet in acidic FX solution.

Many materials used for dosimetry, absorb water readily. The effects of humidity on the response of many solid high dose dosimetry systems have been investigated [2,3,4,5,6,7,8]. Failure to take effects of moisture content into account can lead to large uncertainties in dose estimation, as found in the case of Red Perspex dosimeters. Careful packaging however protects the dosimeters against changes in relative humidity and is essential for the performance of some Radio chromic and plastic dosimeters [9,10,11]. Effect of relative humidity on glycine powder is well studied and was found that the gamma dose response of glycine is stable in the relative humidity range of 0 to 35 % [12]. Since glycine pellets were fabricated without using any binder or effervescent agent, study on effect of humidity on glycine powder was considered to hold true for these pellets. However sodium bicarbonate is hygroscopic in nature and its inclusion in glycine pellet would significantly affect the dose response for varied humid conditions. Hence effect of relative humidity on effervescent glycine pellets was carried out in the present work.
2. EXPERIMENTAL

Glycine was obtained from Merck, Germany and xylenol orange (XO) from Loba Chemie, Austria. All other reagents used were of Analytical Reagent grade. FX solution was prepared in singly distilled water.

Glycine and sodium bicarbonate in the ratio 8:1 were mixed thoroughly in a lab scale vibration mill for a period of 5 mins. Glycine pellets were further fabricated using the dry compression technique by means of a manual hydraulic KBr press having maximum capacity of 15 Tons. Using this press, a 5 ton force was applied on homogenous powder mixture of glycine and sodium bicarbonate placed in a tungsten carbide die having diameter of 13 mm.

To check the consistency in dimension and weight, pellets were selected randomly. Dimension i.e. diameter and thickness of the glycine pellets was determined by using a digital vernier caliper. Weight of the pellet was determined using an accurate digital semi-micro balance (Sartorius make; Germany). Friability test of glycine pellets was carried out using single drum digital friabilator (Veego, India) as per the recommended operating procedure [3]. Twenty pellets were weighed and used for the test. Pellets were removed after performing 100 rotations of the drum at a constant speed of 25 rotations per minute. These pellets were reweighed. Care was taken to remove the adhering dust prior to weighing. Hardness test of glycine pellets was carried out using Physer type hardness tester (Shital Industries, India). This test was performed as per the recommended operating procedure [13]. For carrying out this test, twenty pellets were selected randomly.

Gamma Chamber – 900 was used for dose response calibration of the glycine pellet system. Irradiations were done at the center position of the irradiation volume. This position was calibrated in terms of dose-rate by using Fricke dosimeter, which is a reference standard dosimeter [14].
Figure 1: (1A) Irradiation set-up for dose rate calibration using Fricke dosimeter
(1B) Set-up for irradiation of glycine pellet at calibrated position

Specially designed perspex stand as shown in Fig. 1A was used for providing reproducible irradiation geometry, which was used for calibration of center position of irradiation volume of gamma chamber–900. During irradiation, each pellet was placed in perspex dosimeter container having 4 mm wall thickness which served as the necessary build-up for achieving electronic equilibrium [15] as shown in Fig. 1B.

A Jasco V 530 UV / Vis double beam spectrophotometer was used for the absorbance spectra measurements and for absorbance measurements at a fixed wavelength using 10 mm cuvette. Irradiated / unirradiated effervescent glycine pellet was transferred to pre-cleaned weighing bottles containing 10 mL of FX solution. Absorbance of irradiated glycine / FX and unirradiated glycine / FX solutions was done against air as reference. Net change in absorbance of unirradiated glycine / FX solution (control) from the absorbance of irradiated glycine / FX solution was calculated. Absorbance measurements of Fricke dosimeters were done as per the recommended procedure [14].

All glasswares, dosimeter containers, build-up tubes and perspex spacers used were cleaned as per the recommended procedure [16]. Fabrication of pellets does not produce significant amount of free radicals to affect its response as was evident from earlier studies [1], hence pellets were used immediately after fabrication for determining the optimum composition of FX solution, and were irradiated as mentioned earlier to a dose of about 770 Gy. Optimum acid concentration required in FX solution for obtaining the maximum net absorbance was determined by adding 10 mL of FX solution containing 2 \times 10^{-4} \text{ mol dm}^{-3} of ferrous ammonium sulphate and 2 \times 10^{-4} \text{ mol dm}^{-3} of XO at different sulphuric acid concentrations ranging from 0.220
to 0.300 mol dm$^{-3}$, to irradiated and unirradiated pellet. The absorbance spectra of unirradiated / irradiated pellet in FX solutions at different acidities were scanned over a wavelength range of 500 - 600 nm against air as the reference. The absorbance spectrum of unirradiated pellet in FX was subtracted from that of irradiated glycine in FX, for all the acidities. The subtracted spectra i.e. the net spectra were thus obtained. Optimum XO concentration for obtaining the maximum absorbance value; was determined by adding 10 mL FX solution containing 2 x 10$^{-4}$ mol dm$^{-3}$ ferrous ammonium sulphate and 0.265 mol.dm$^{-3}$ sulphuric acid at different XO concentrations ranging from 0.6 to 1.1 x 10$^{-4}$ mol dm$^{-3}$, to irradiated / unirradiated pellet. The effect of concentration of ferrous ions on net absorbance value was studied by adding 10 mL FX solution containing 0.9 x 10$^{-4}$ mol dm$^{-3}$ XO and 0.265 mol dm$^{-3}$ sulphuric acid at different ferrous ion concentrations ranging from 0.5 to 7.0 x 10$^{-4}$ mol dm$^{-3}$, to irradiated / unirradiated pellet.

Change in absorbance with time was determined as follows: Pellets were irradiated as mentioned earlier to dose of 175 Gy. FX solution containing 4.0 x 10$^{-4}$ mol dm$^{-3}$ ferrous ions, 0.9 x 10$^{-4}$ mol dm$^{-3}$ XO and 0.265 mol dm$^{-3}$ sulphuric acid, was prepared by dissolving 0.15686 g of ferrous ammonium sulphate and 0.06840 g of xylenol orange in 1L of 0.265 mol dm$^{-3}$ sulphuric acid. Irradiated and unirradiated pellets were dissolved in FX solution having optimum composition and the net absorbance values at 547 nm were recorded at regular interval of time over a period of about 130 minutes. Absorbance measurements were done against air as the reference using 10 mm cuvette and net absorbance values determined.

Dose response curve for the glycine pellets was obtained as follows: Pellets were irradiated to different doses ranging from 100 to 1400 Gy. For each dose point two pellets were irradiated. 10 ml of FX solution having optimum composition was added to pre-cleaned weighing bottles each containing irradiated / unirradiated pellet. All absorbance measurements were carried out using 10 mm cuvette at 547 nm. Average control absorbance value i.e. Unirr – FX, was calculated from absorbance of set of five FX solutions containing unirradiated glycine. The net absorbance, ∆A i.e. Absorbance (Irr – FX) – Average absorbance (Unirr – FX), was then determined. The average net absorbance, standard deviation and coefficient of variation were further calculated for respective doses and the average net absorbance values were plotted against the respective dose values.

For determining the effect of relative humidity during pre-irradiation storage of glycine pellets, twenty five pellets were kept in a pre-cleaned petri dish and placed inside a desiccator containing the required saturated salt solution in order to establish various RH in the range 12 to 97% [12]. Table 1 shows the list of salts used for this purpose. RH was measured using a digital hygrometer with an in-built temperature sensor. 0 % RH was obtained by using dried silica gel.
Table 1: Saturated salt solutions for obtaining the desired RH in a closed container

<table>
<thead>
<tr>
<th>Saturated salt solution</th>
<th>Relative humidity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Chloride monohydrate</td>
<td>12.4</td>
</tr>
<tr>
<td>Magnesium Chloride Hexahydrate</td>
<td>33.6</td>
</tr>
<tr>
<td>Magnesium Nitrate Hexahydrate</td>
<td>54.9</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>75.5</td>
</tr>
<tr>
<td>Potassium Sulphate</td>
<td>97.0</td>
</tr>
</tbody>
</table>

Figure 2 shows the set-up for conditioning glycine to various RH conditions ranging from 0 to 97%. For each RH, glycine was conditioned for a period of 48 hrs. Pre-irradiation and post-irradiation storage conditioning of pellets to varied humidity was conducted at ambient temperature of laboratory i.e. about 25 °C. To obtain reproducible dose response three sets each containing three pellets were irradiated to three different doses covering the entire dose range of the pellet system, viz.: 125, 500 and 900 Gy. Irradiation set-up was similar to that shown in Fig. 1B. Absorbance measurements were done as mentioned earlier and net absorbance values were calculated. The average of net absorbance values for each dose was then calculated. Relative variations in average net absorbance for respective doses at different relative humidities were normalized to that at 0% relative humidity.

Figure 2: Set-up for conditioning of glycine powder to desired RH

For determining the effect of relative humidity during irradiation, pellets were prepared as explained earlier. The set-up for irradiating glycine pellets at required relative humidity consisted of an air-tight plastic container. At the bottom center of this container, a perspex base along with the build-up was glued in order to obtain reproducible irradiation geometry. Saturated salt solution for providing the desired
relative humidity was kept surrounding this base. Glycine pellet was inserted in the dosimeter container having 13.3 mm i.d., 10 mm height and 4 mm wall thickness. The pellet was placed at the center of the air-tight container by means of a perspex spacer having 13.3 mm diameter and 27 mm height. The lid of this container was closed and kept in ambient temperature condition (~25°C) prevailing in the laboratory for 48 hrs. Entire set-up was then placed in the irradiation volume of Gamma Chamber - 900 for irradiation, as shown in Fig. 3.

1 Irradiation volume of GC 900, 2 Glycine pellet in dosimeter container, 3 Perspex spacer, 4 Lid of container, 5 Plastic container, 6 Perspex jig, 7 Saturated salt solution

**Figure 3:** Set-up for irradiating glycine pellet at desired relative humidity

This set-up was initially calibrated in terms of dose rate at its center position using Fricke dosimeter [14]. This calibrated center position along with the jig was used for irradiation of dosimeters at the desired RH. Irradiation temperature was about 29°C. Three pellets were irradiated for each of the doses viz.: 125, 500 and 900 Gy. Absorbance measurements were carried out and the net absorbance values were calculated. The average net absorbance values for respective doses for different relative humidities were calculated. Relative variations in average net absorbance for respective doses at different relative humidities were normalized to that at 0% relative humidity.

For determining the effect of relative humidity during post-irradiation storage, glycine pellets were irradiated and conditioned to the desired relative humidity. During conditioning, pellets remained packed inside the dosimeter containers. The purpose of this study was find out the effect of relative humidity on dose response due storage of irradiated pellets in different relative humidity after irradiation. Three pellets were irradiated for each dose point. Absorbance measurements were done and net absorbance values for each dose point at various relative humidities were
calculated. Relative variations in average net absorbance for respective doses at different relative humidities were normalized to that at 0% relative humidity.

3. RESULTS AND DISCUSSION

Glycine 400 mg effervescent pellets were fabricated using dry compaction technique without any binder. Sodium bicarbonate was used as effervescent agent. The average diameter, thickness and weight of hundred pellets were found to be $13.17 \pm 0.07$ mm, $2.09 \pm 0.01$ mm and $425.45 \pm 0.13$ mg, respectively. Friability i.e. the difference between weight of the pellets before and after 100 rotations, for twenty pellets was found to be less than 0.5%. Average hardness value for twenty-five pellets was found to be $15.41 \pm 0.58$ kg. Statistical variation in diameter, thickness, weight, friability and hardness for these pellets satisfy the essential physical parameters required for ease of handling of a routine dosimeter. Also due to effervescent agent in the pellet, complete dissolution of pellet in FX solution can be obtained within 30 s.

Effect of sulphuric acid concentration on the net absorbance values at different wavelengths was studied and is as shown in Fig. 4. It is clear from the figure that the maximum net absorbance occurs at $0.25 \text{ mol dm}^{-3}$ of acid concentration and the wavelength of maximum absorbance ($\lambda_{\text{max}}$) is 547 nm.

![Figure 4: Effect of acidity on dose response at different wavelengths](image)

As dose response is dependent on composition of FX solution, optimum FX composition was established and was found to be $4.0 \times 10^{-4}$ mol dm$^{-3}$ ferrous ammonium sulphate, $0.9 \times 10^{-4}$ mol dm$^{-3}$ xylene orange and $0.265$ mol dm$^{-3}$ sulphuric acid, as shown in Fig. 5.
Figure 5: Optimum FX composition: (a) Dose response at different sulphuric acid concentration, (b) Effect of xylenol orange concentration on dose response, (c) Effect of ferrous ion concentration on dose response.

Figure 6 shows the change in the net absorbance over different interval of time after dissolution. It was found that the net absorbance value initially increases continuously due to slow oxidation reactions leading to ferric formation for a period of about 30 minutes; and then it remains almost constant for a period of at least 90 minutes.
Figure 6: Net absorbance change after dissolution of glycine pellet in FX

Figure 7 shows the plot of response Vs dose for the pellets. Graph obtained is non-linear with 3\(^{rd}\) order polynomial fit. The overall reproducibility for response for any dose was found to be within ±2 % which is as illustrated in the form of bars in the Fig. 7 for response variation for each dose. Also it is clear that this system has a useful dose range of 100 to 1000 Gy.

Figure 7: Dose response of effervescent glycine pellets
Gamma dose response of effervescent glycine pellet is dependent on RH prevailing during the storage of mixture of glycine and sodium bicarbonate. Figure 8 shows the plots of relative variation in average net absorbance for different doses normalized to that at 0% relative humidity vs relative humidity prevailing during pre-irradiation storage of pellets. Dose response remains constant in the RH range 0 to 12% but thereafter it decreases with increase in RH, as shown in Fig.8.

Glycine and sodium bicarbonate are both hygroscopic and hence the effervescent pellet can absorb ambient moisture with increase in RH thus increasing its water content, further destroying the radiation-induced free radicals, decreasing the dose response. It is obvious from Fig. 8 that decrease in dose response with increase in RH would be prominent for temperatures such as 0, 10 or -10°C due to condensing humidity, as studied for glycine pellets without sodium bicarbonate [12]. As no salt was available to condition the pellets to relative humidity in the range between 0 to 12%, it would have point less to study for lower temperatures such as 10, 0 or -10°C. Hence after fabrication of these pellets it is recommended to immediately store the pellets in air-tight sealed bottle kept in a desiccator containing dry silica gel, in order to maintain the relative humidity close to 0%.

![Figure 8: Influence of pre-irradiation RH conditions on dose response at different temperatures](image)

Figures 9 & 10 represent the plots of relative variation in average net absorbance for different doses normalized to that at 0% relative humidity vs relative humidity prevailing during irradiation and post-irradiation storage of pellets.
It is clear from Figs. 9 & 10, that the maximum relative variation normalized to that at 0% relative humidity is ± 2%, further indicating that the dose response of these pellets is independent of humidity prevailing during irradiation and post-irradiation storage of glycine. This behaviour can be attributed to the fact that prior to irradiation; pellet is placed in a dosimeter container which provides adequate barrier from the ambient moisture. As a result once the pellet is placed in the dosimeter container, it becomes immune to the effect of relative humidity.
4. CONCLUSION

Fast dissolving pellets were fabricated using sodium bicarbonate as an effervescent agent. As sodium bicarbonate is hygroscopic, study of effect of relative humidity on dose response of these pellets was carried out. It is recommended that these pellets prior to irradiation should be stored in relative humidity of 0 to 12% so that its response is not affected by humidity. Also it is concluded that humidity has no effect on the dose response of these pellets during and post-irradiation conditions. Hence these pellets along with spectrophotometric read-out method can be used for measuring a useful dose range of 100 to 1000 Gy, which is apt for routine dosimetry in low dose applications of radiation processing.

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