Characterization of lithium diborate, sodium diborate and commercial soda-lime glass exposed to gamma radiation *via* linearity analyses

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ABSTRACT

The linearity characteristic in radiation dosimetry presents a growing interest. Glasses have been applied to high radiation doses. In this work, materials will be analyzed and compared in relation to their linearity ranges. Lithium diborate, sodium diborate and commercial glass were irradiated with doses from 10 Gy to 10 kGy using a ^{60}Co Gamma-Cell system 220 and evaluated with the UV–vis technique. The sensitivity analyses were applied through four methodologies, searching for linear regions in their response. The results show that all four applied analyses indicate linear regions for the tested radiation detectors. The materials with higher linearity range, in descending order, were lithium diborate, sodium diborate and commercial soda-lime glass. The radiation detectors present potential use for radiation dosimetry in intermediate and high doses.

1. Introduction

The search for new materials that can be used as radiation detectors is of great technological importance. This is especially true in the food industry and medicine, where there are large demands for obtaining measurements *in situ,* often impossible due to the fragility and size of the conventional sensors (Fedorov and Viskanta, 2004; Keeffe et al., 2008; Kowatari et al., 2016; Oliveira et al., 2018). The employment of sensor elements based on ceramic, glass and/or glass-ceramics is interesting due to their low production costs and to their good mechanical properties. Glasses become of interest to be used as active elements in gamma ray sensors due to their changes in the optical spectra when exposed to gamma radiation (Ehrt and Vogel, 1992; Sheng et al., 2009; Kaur et al., 2014).

Numerous authors have tried to explain the mechanism by which glasses become colored in the presence of gamma radiation (Bishay, 1970; Abbas and Ezz-Eldin, 1994; Rojas et al., 2006; Baydogan and Tugrul, 2012; Du et al., 2013; Maeder, 2013; Kaur et al., 2014). The ionizing radiation induces characteristic absorption bands in the glass samples depending on the irradiation conditions. There is a variation in color due to the exposure to radiation. The color change is believed to be related to the oxidation mechanism which may create color centers that can absorb light (Baydogan and Tugrul, 2012).

One explanation for the formation of color centers is credited to the production of electron-hole pairs, which then may be individually trapped in numerous local defects in the glass structure (Abbas and Ezz-Eldin, 1994). However, the increase in optical density with increasing gamma radiation dose is also attributed to the presence of impurities inherent in the glass, such as the ratio Fe^{3+}/Fe^{2+}. Therefore, the full understanding of the real effect of the gamma radiation exposure of the glass is still the subject of studies, and it remains without a definitive explanation (Quezada and Caldas, 1999; Rodrigues and Caldas, 2002; Caldas and Teixeira, 2002; Bahri et al., 2014)

In this work, the UV–vis spectrophotometry, a non-destructive technique, was applied to study the color centers of the gamma irradiated glass samples. The linearity analysis was utilized, and it can be viewed as the characterization of the possible sensor transfer function (Wyatt, 1978). The glass compositions used for the irradiation studies were commercial soda-lime, and lithium and sodium diborate.

2. Materials and methods

The glass samples of lithium diborate and sodium diborate, and of commercial soda-lime glass have dimensions of $1 \times 1 \times 4$ mm^3. They were irradiated with absorbed doses between 10 Gy and 10 kGy using a ^{60}Co Gamma Cell-220 system (dose rate of 1.089 kGy/h). A spectrophotometer Genesys 10S/Thermo Scientific was used for response evaluation. The spectra were obtained for wavelengths from 190 to

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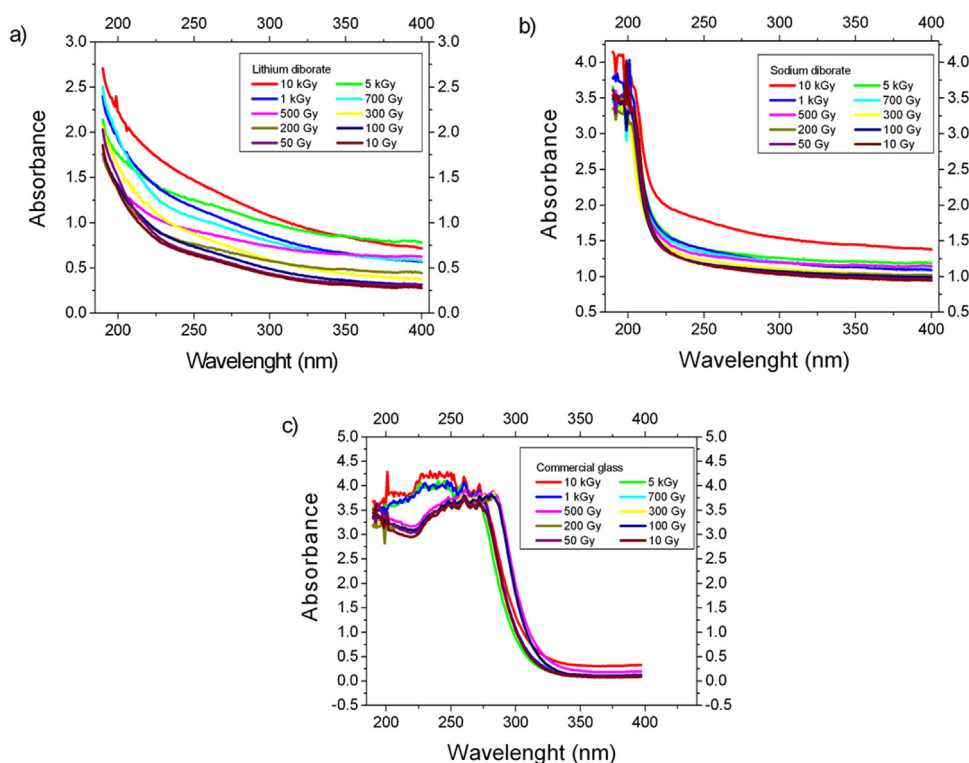
Fig. 1. UV–vis spectra for glass samples irradiated with absorbed doses from 10 Gy to 10 kGy (^{60}Co source): absorbance *versus* wavelength. a) lithium diborate; b) sodium diborate and c) commercial soda-lime glass. The average of 3 samples was evaluated for each curve, and the uncertainty obtained was lower than 1%.

400 nm, a scanning interval of 1 nm, and a spectral band of 1.8 nm. Nine samples without irradiation were evaluated for reference measurements and 30 samples were irradiated, triplicates were made for each absorbed dose. The parameters for the irradiation procedure were: source-detector distance of 15 cm, maximum dose depth of 3.0 mm; the glasses were placed in front of an acrylic cylinder with 6.4 mm of diameter and 20 cm of height.

Linear relationships establish some useful properties that are important to model properly physical systems, which are easy to perform analyses on the model dynamics, supplying mathematical interpretations towards the experimental data that obey the linear relations. These properties include associative, cumulative and superposition features, which reinforce the capabilities to predict and extrapolate new values, based only in a few measurements of the planned experiment. As an example, this is suitable and useful when trying to predict the absorbed dose in biological tissue at high dose rates, since its rapid response fading cannot allow properly prediction of the effect of the color changing of the sample as function of the absorbed dose.

Then, to assess linear relationships among experimental results, the linear regression technique appears as the most used, consisting on the analytical implementation of the Least Square Residual Minimization Method (Montgomery et al., 2012). Then, the linear regression uses the explanatory variable and the independent variable to create a linear model, based on some measured values of the explanatory variable, x, and its respective response on the independent variable, y. This method consists in y to be any outcome, and x to be any explanatory variable, and then it may possible express the structural model using Eq. (1):

$$E(y|x) = \beta_0 + \beta_1 x \tag{1}$$

where E ("the expected valued") indicates a population mean; $y|x$, which is read "y given x", indicates the possible values of y when x is restricted to a single value; and β_0, read as "beta zero", is the intercept parameter; and β_1, read as "beta one", is the slope parameter.

In this work, the linear regression was applied to evaluate the possible linear relations established into a multivariable system,

counting with two input variables and one response. The system consisted to verify the linear response of the absorbance of the Lithium and Sodium Diborate, and Soda-lime commercial glasses, irradiated with gamma rays, which will allow measuring the linear behavior of absorbance in each of these glasses under irradiation procedures. The first input variable was the wavelength spectrum, between 290 and 400 nm, and the second response was discrete absorbed dose, varying discretely: 10 Gy, 50 Gy, 100 Gy, 200 Gy, 300 Gy, 500 Gy, 700 Gy, 1 kGy, 5 kGy and 10 kGy. The response was the spectral absorbance measured as function of wavelength and absorbed dose then making a two input system, or multivariable system.

Nevertheless, before the implementation of the linear regression, the variable reduction of the system was first performed, to reduce the multivariable regression into a single variable regression, using the area Under the Curve Method (UCM) and the Wavelength Method (WM), and similar procedure can be used performing a Principal Component Analysis (PCA). In addition, in this work, the accuracy comparison between the area Under the Curve and the Wavelength Methods was made. Basically the area Under the Curve Method calculates the area under the curve of the absorbance from each one of the discrete absorbed dose as function of wavelength; each integral area consisted of a point, at the graph of Integral Area *versus* Absorbed Dose; then a linear regression is performed. Alternatively, the Wavelength Method only takes a wavelength at a time and uses as the single absorbance response associated from discrete absorbed dose to create a graph of Absorbance *versus* Absorbed dose; then a linear regression is applied.

An innovation of this work consists to evaluate the Wavelength Method over all points from 290 nm up to 400 nm, with the optical step of 1 nm, then making possible to find the best optimal wavelength automatically. This was made, using a Matlab script configured to perform a linear regression and to save the Person R^2 correlation index, that allows a quick inspection of the linearity of the linear regression, since a R^2 value nearest to the unity shows a more linear model. Otherwise, the same occurs from the area Under the Curve Method. In addition, to get a comparison on the linear response of all three glasses,
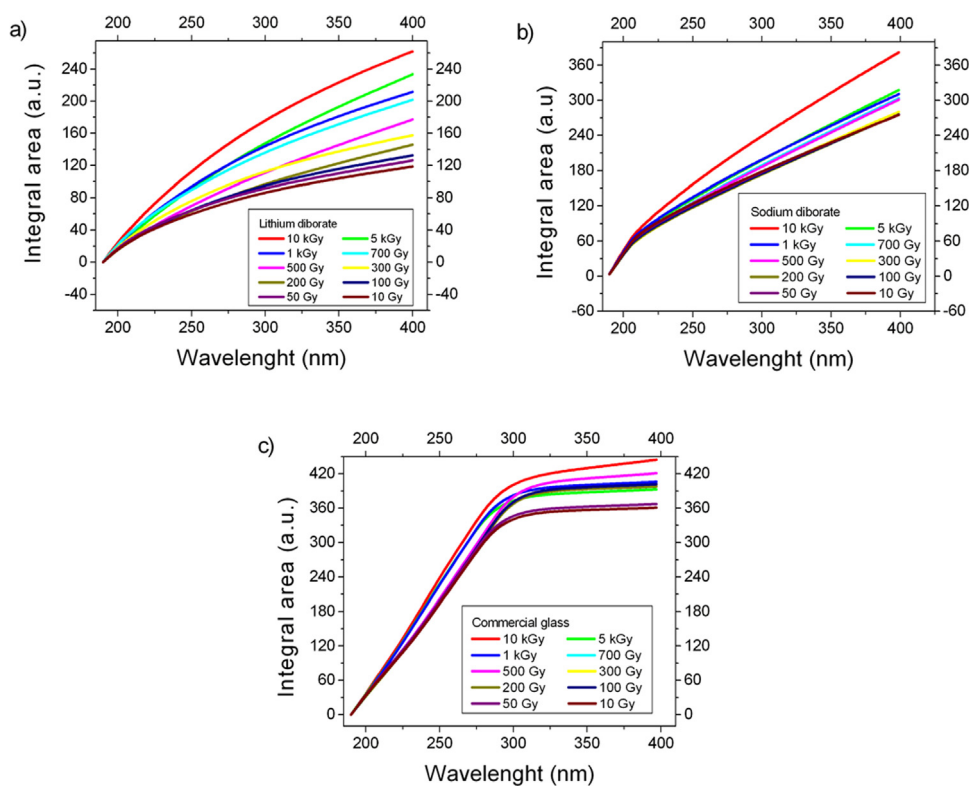
Fig. 2. Integral area for spectra for glass irradiated *versus* wavelength, using the UV–vis technique and irradiation from 10 Gy up to 10 kGy of absorbed doses (^{60}Co source) for: a) lithium diborate; b) sodium diborate; and c) commercial soda-lime glass.

the cumulative probability curve from the linearity result expressed by the R^2 was implemented using the Matlab; this cumulative probability curve was built since the R^2 date were assumed within a Gaussian distribution.

3. Results

The spectra of all these materials show in Fig. 1 absorbance values associated to the absorbed doses received by the samples. These results show that it is possible to use the UV–vis technique to determine if the glass samples were irradiated or not. The color variation in relation to absorbed dose was verified and indicates that the glasses may be used as YES/NO dosimeters.

The results were divided in two parts, the first part with analyses of area Under the Curve Method and the second part with the Wavelength Method, both used to evaluate the linearity performance of the lithium diborate, sodium diborate and the commercial soda-lime glass samples.

In Fig. 2, the integral area from Fig. 1 curves *versus* wavelength of the three materials are shown. These results indicate in which region of the wavelength polynomially occurs; in this case, for lithium diborate between 250 nm and 400 nm, for sodium diborate between 220 nm and 400 nm, and for commercial soda-lime glass between 190 nm and 270 nm.

The integral areas of the material absorbance curves *versus* absorbed dose are shown in Fig. 3. For lithium diborate samples, there is linearity up to 1 kGy and another linear region between 1 kGy and 10 kGy; for sodium diborate sample a linear region between 10 Gy and 1 kGy can be observed, and for commercial soda-lime glass the linear region occurs between 10 Gy and 100 Gy, and then a non-linear region between 500 Gy and 10 kGy. Then, on the first linear regions from 10 Gy to 1 kGy, a regression procedure was applied, obtaining R^2 values of 0.98336, 0.95957 and 0.25882 for lithium diborate, sodium diborate and commercial soda-lime samples respectively. These values show that using the Area Under the Curve Method the lithium and sodium

diborate samples present potential use as dosimeters, but the soda-lime glass samples do not, due to their lower linearity (very low R^2 value).

In Fig. 4 are presented the dose-response curves (at 250 nm) of all materials, exposed to gamma radiation (^{60}Co sources). The results show that lithium diborate response presents the best linearity behavior up to 1 kGy. The materials of lithium diborate, sodium diborate and commercial soda-lime glass samples, have R^2 linearity coefficients of 0.9888, 0.9843 and 0.6316 respectively. In this case, the nonlinear behavior of the commercial soda-lime glass is evidenced, being practically linear only in the region up to 500 Gy.

Fig. 5a shows the linearity as a function of wavelength, associated to all absorbed doses of the dosimeters, using the Wavelength Method, to produce the regression and from it acquire the linearity R^2 value. It should be noted that the dosimeter closest to the linearity (nearest to 1) in the entire region of the analyzed spectrum 190–400 nm is lithium diborate, followed from sodium diborate and commercial soda-lime glass. The region between 225–275 nm indicates the region with the highest sensitivity for linearity for the dosimeters lithium diborate, sodium diborate and commercial soda-lime glass, respectively.

The cumulative probability as a function of linearity may be observed in Fig. 5b, in which the best dosimeter in terms of linearity can be identified. By inspection on the cumulative probability, it is possible to affirm that the lithium and sodium diborate samples present 90% linearity, greater than 0.80 and 0.73 respectively over the range of 190–400 nm. On the other hand, only 10% of the samples of the wavelength in the soda-lime has linearity above 0.60, showing therefore that the commercial soda-lime glass is not recommended for use as dosimeter. It must be noted at the specific wavelength that the lithium and sodium diborate samples show linearity close to the unity, with potential use as dosimeters.

Finally, comparing the area Under the Curve and the Wavelength Methods, they showed good agreement, since both ranked the lithium diborate material as the most promisor dosimeter followed by the sodium diborate material; in addition, both methods showed that the
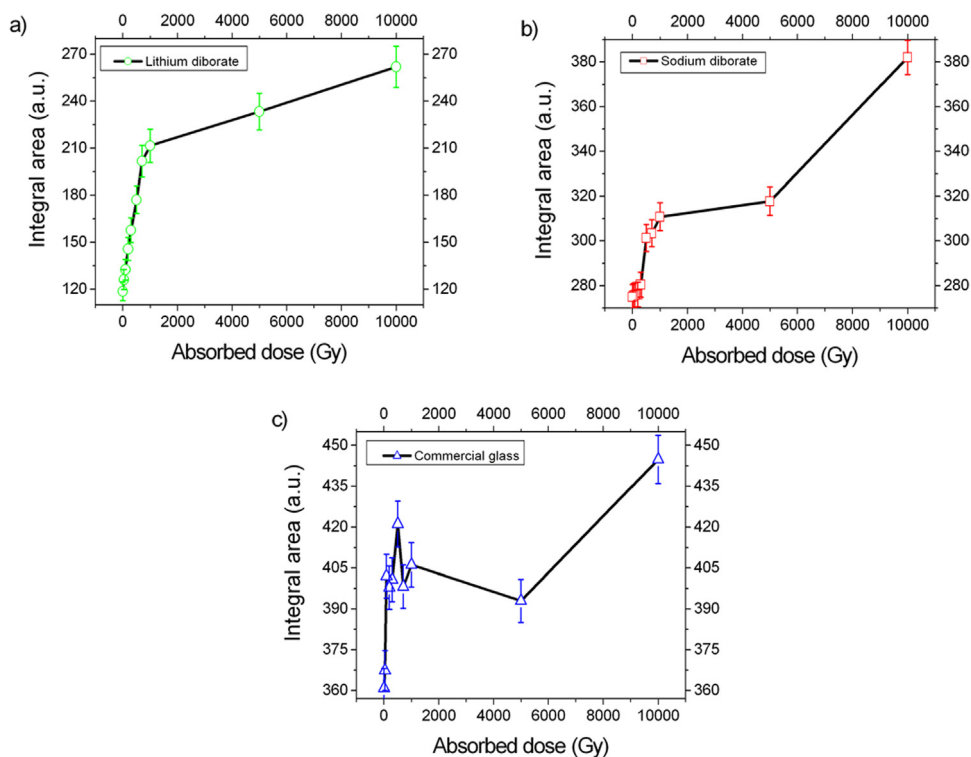
Fig. 3. Integral area of the material absorbance curves *versus* absorbed dose, using the UV–vis technique and wavelength interval from 190 nm up to 400 nm for: a) lithium diborate; b) sodium diborate and c) commercial soda-lime glass.
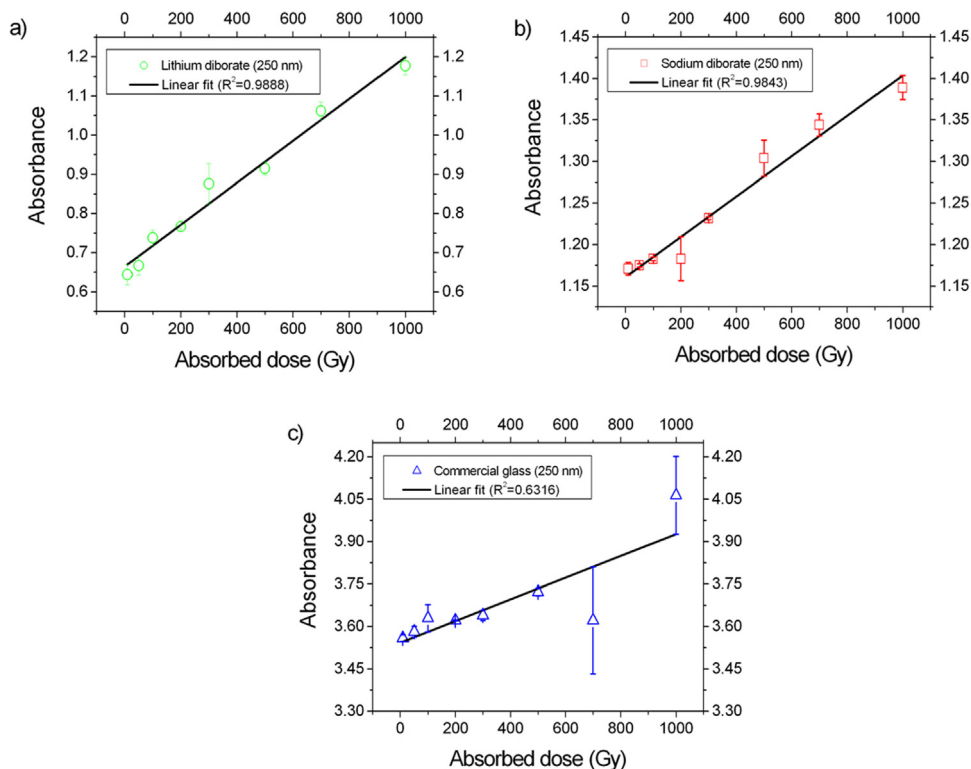

Fig. 4. Dose-response curves of the glass samples (^{60}Co source) for 250 nm: a) lithium diborate; b) sodium diborate and c) commercial soda-lime glass.

commercial soda-lime glass does not present good dosimetric properties.

Another material, Ethylene Vinyl-Acetate Copolymer (EVA), presented also a linear relationship with the absorbed dose (Oliveira et al., 2018).

4. Conclusions

The UV–vis spectra lithium borate, sodium diborate and commercial glass samples were obtained. The UV–vis measurements may be useful in gamma radiation dosimetry, using the spectra of irradiated glasses;
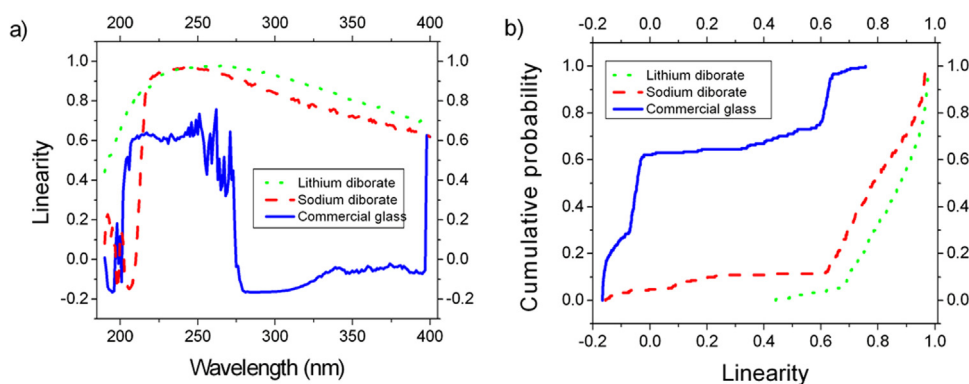
Fig. 5. Linearity analyses of lithium diborate, sodium diborate and commercial glass: a) Linearity *versus* wavelength; and b) Cumulative probability *versus* linearity.

the dose-response curves showed good linear relationships at 250 nm; the highest linearity was shown in order respectively for lithium borate, sodium diborate and commercial glass; the glass samples changed their coloration proportional to the absorbed doses, and they may be used as Yes/No detectors.

Acknowledgments

References

Abbas, A.F., Ezz-Eldin, F.M., 1994. Optical absorption of some gamma-irradiated lithium-boro-silicate glasses doped with some rare-earth metal oxides. Nucl. Instrum Methods 93, 457–463.

Bahri, T.N.H.T.K., Wagiran, H., Hussin, R., Hossain, I., Kadni, T., 2014. Thermoluminescence properties of CaO-B_2O_3 glass system doped with GeO_2. Radiat. Phys. Chem. 102, 103–107.

Baydogan, N., Tugrul, A.B., 2012. Borosilicate glass for gamma irradiation fields. Solid State Sci. 14, 1692–1697.

Bishay, A., 1970. Radiation induced color centers in multicomponent glasses. J. Non-Cryst. Solids 3, 54–114.

Caldas, L.V.E., Teixeira, M.I., 2002. Commercial glass for high doses using different dosimetric techniques. Radiat. Prot. Dosim. 101, 149–152.

Du, J., Wu, J., Zhao, L., Song, L., 2013. Color centers of a borosilicate glass induced by 10 MeV proton, 1.85 MeV electron and ^{60}Co-γ ray. Radiat. Phys. Chem. 86, 59–63.

Ehrt, D., Vogel, W., 1992. Radiation effects in glasses. Nucl. Instrum. Methods Phys. Res. B 65, 1–8.

Fedorov, A.G., Viskanta, R., 2004. Radiation characteristics of glass foams. J. Am. Ceram. Soc. 83, 2769–2776.

Kaur, R., Singh, S., Pandey, O.P., 2014. UV–vis spectroscopic studies of gamma irradiated lead sodium borosilicate glasses. J. Mol. Struct. 1060, 251–255.

Keeffe, S.O., Fitzpatrick, C., Lewis, E., Alâ, A.I., 2008. A review of optical fibre radiation dosimeters. Sens. Rev. 34, 136–142.

Kowatari, M., Kubota, T., Shibahara, Y., Fujii, K., Takamiya, K., Mizuno, S., Yamana, H., 2016. In situ environmental radioactivity measurement in high-dose rate areas using a CdZnTe semiconductor detector. Radiol. Issues Fukushima's Revital. 11, 121–131.

Maeder, T., 2013. Review of Bi_2O_3 based glasses for electronics and related applications. Int. Mater. Rev. 58, 3–40.

Montgomery, C.D., Peck, E.A., Vining, G.G., 2012. Introduction to Linear Regression Analysis. Wiley, New Jersey, USA.

Oliveira, L.N., Nascimento, E.O., Schimidt, F., Antonio, P.L., Caldas, L.V.E., 2018. Assessment of ethylene vinyl-acetato copolymer (EVA) samples bombarded by gamma radiation via linearity analyses. J. Phys. Conf. Ser. 975, 1–4.

Quezada, V.A.C., Caldas, L.V.E., 1999. Glass detectors for dose determination in a flower irradiation process. Radiat. Prot. Dosim. 85, 473–475.

Rodrigues Jr, A.A., Caldas, L.V.E., 2002. Commercial plate window glass tested as routine dosimeter at a gamma irradiation facility. Radiat. Phys. Chem. 63, 765–767.

Rojas, S.S., Yukimitu, K., de Camargo, A.S.S., Nunes, L.A.O., Hernandes, A.C., 2006. Undoped and calcium doped borate glass system for thermoluminescent dosimeter. J. Non-Cryst. Solids 352, 3608–3612.

Sheng, J., Wu, Y., Yang, X., Zhang, J., 2009. UV-laser irradiation on the soda-lime silicate glass. Int. J. Hydrog. Energy 34, 1123–1125.

Wyatt, C.L., 1978. Radiometric Calibration: Theory and Methods. Academic Press, New York, USA.