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Dosimetric characteristics of different types of saccharides: An EPR and UV spectrometric study

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ABSTRACT

The time stability and dose response of the free radicals produced in various types of “less-studied” mono- and disaccharides by γ-radiation is studied by EPR (Electron Paramagnetic Resonance) and UV spectrometry. The time evolution of the shape of the EPR spectra of irradiated saccharides is investigated from 5 min to 5 months after irradiation. The intensity of the stable EPR signal is studied as a function of the absorbed γ-dose in the range 0.5–20 kGy. Aqueous solutions of irradiated solid saccharides exhibit a UV absorption maximum in the range 250–290 nm. A linear dependency is found between the magnitude of the UV absorption maximum and the absorbed γ-dose. The time stability of the UV absorption maximum is also studied for every saccharide. The results are compared with those obtained for irradiated sucrose.

1. Introduction

Ionizing radiation has wide applications in many fields of human activity, for example in therapy of certain human diseases or in sterilization of foodstuffs and medical consumables. Its destructive nature is, however, connected with some health risks for people who are working with it or are exposed to it in radiation accidents. A good, reliable dosimetric system is therefore needed. In the last decades many studies suggest sucrose as one of the most promising materials for regularly and emergency EPR dosimetry. It is of special interest for nuclear emergency dosimetry because of its widespread use, high radiation sensitivity and stability of the radiation-induced free radicals (Nakajima, 1988; Nakajima and Otsuki, 1990; Trivedi and Greenstock, 1993). The sugar/EPR dosimeter has potential for detection of not only X and γ-radiation but also of heavy particle radiation (Nakagawa, 2000; Nakagawa and Nishio, 2000; Nakagawa and Sato, 2002, 2004, 2005; Karakirova et al., 2008). Recently, it was shown that aqueous solutions of γ-irradiated saccharides exhibit specific absorption bands in the UV range 240–260 nm whose intensity is linearly dependent on the absorbed dose (Yordanov et al., 2002; Yordanov and Georgieva, 2004; Yordanov and Karakirova, 2007a). Moreover, a linear relation was also found between the EPR signal intensity of a solid sample and the UV absorption intensity of its aqueous solution, thus opening new possibilities of calibrating EPR spectra by means of UV spectrometry (Yordanov and Karakirova, 2007b). Very recent studies (Karakirova et al., 2008; Yordanov and Karakirova, 2007a, b) have shown that combining the EPR and UV response of sucrose samples irradiated with γ-photons or C, N and Si particles can be used for discriminating the nature of the radiation.

The aim of the present paper is to extend the previous studies by investigating the potential of various other types of mono- and disaccharides as EPR and UV dosimeters for γ-radiation. Most of the saccharides investigated in this work have never before been considered for dosimetric purposes.

2. Experimental

2.1. Materials

All saccharides listed below and used for the present study (see Fig. 1 for their chemical structure) were purchased from Aldrich.

Monosaccharides: β-D-arabinofuranose (arabinose), β-D-ribofuranose (ribose), α-D-galactopyranose (galactose), α-D-sorbopyranose (sorbose)

Disaccharides: α-D-glucopyranosyl (1–1) α-D-glucopyranoside (trehalose), β-D-galactopyranosyl (1–4) α-D-glucopyranose (lactose) and α-D-glucopyranosyl-(1↔2)-β-D-fructofuranoside (sucrose).

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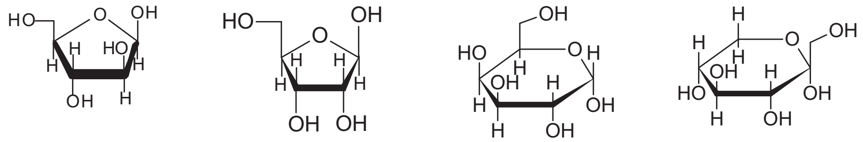
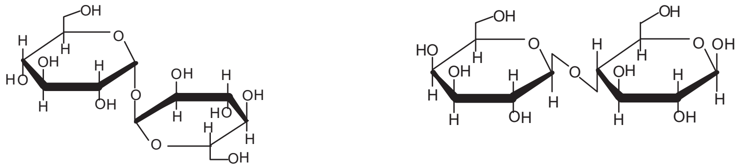
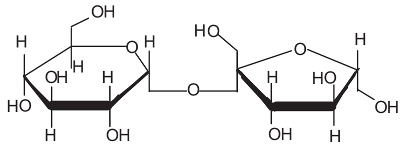


β-D-arabinofuranose (arabinose) β-D-ribofuranose (ribose) α-D-galactopyranose (galactose) α-D-sorbopyranose (sorbose)



α-D-glucopyranosyl (1-1) α-D-glucopyranoside (trehalose) β-D- galactopyranosyl (1-4) α-D-glucopyranose (lactose)



α-D-glucopyranosyl (1↔2) β-D-fructofuranoside (sucrose)

Fig. 1. The chemical structures of the saccharides studied in the present work.

2.2. Preparation of solid state dosimeters

For preparing solid state/EPR (SS/EPR) dosimeters, the saccharides (radiation-sensitive material) were grinded to fine powder under chloroform using an agate mortar in order to avoid the appearance of mechanically induced free radicals (Yordanov and Georgieva, 2004; Yordanov and Karakirova, 2007b). The solvent was evaporated under vacuum, the dry solid material was sieved and only grains with dimension less than 100 mesh were homogeneously mixed with paraffin (binding material) in a ratio 60/40 w/w. The SS/EPR dosimeters were prepared by extruding the homogeneous mixture in the form of cylinders with a diameter and height of 4 and 10 mm.

2.3. Irradiation of the samples

SS/EPR dosimeters and pure powders of all saccharides were irradiated with γ-rays at room temperature using a "Gamma-1300" irradiator (^{137}Cs) at a dose rate of 200 Gy/h in the dose range 0.5–20 kGy. Care was taken that the temperature did not significantly increase by the irradiation. After irradiation all samples were stored in closed plastic bags at room temperature (RT) and shielded from any light source.

2.4. Preparation of samples for UV measurements

Aqueous solutions of the saccharides were prepared by dissolving the solid saccharide powders in distilled water. As previous investigations performed in our laboratory (Yordanov et al., 2002) have shown that the intensity of the UV absorption bands increases linearly with the concentration of the aqueous solution up to 20%, solutions with a concentration of 5% were used in this work. For reference measurements, aqueous solutions were prepared of non-irradiated saccharides with the same concentration.

2.5. Instrumentation

EPR spectra were recorded at RT on an X-band Bruker ER 200D SRC spectrometer operating with a standard (ER4102ST) rectangular (TE_{102} mode) cavity. The cylindrical sample pellets were positioned in quartz sample tubes and shifted up from the bottom with a paraffin separator. The sample tube was fixed each time at the same position in the cavity center. The microwave power and modulation amplitude used in all measurements were 1 mW and 2×10^{-4} T. Charcoal sample was used for calibration of EPR spectrum intensity before each measurement in the kinetic study.

UV measurements were performed on a Specord UV–vis (Carl Zeiss, Jena) spectrophotometer at RT. Quartz sample cells with a path length of 5 mm were used.

Every data point in the kinetic study is the average of measuring at least 3 samples.

3. Results and discussion

3.1. EPR investigation of γ- or X- irradiated solid saccharides

In general, the time stability of radiation-induced EPR signals is an important feature for any EPR dosimeter. Previous work shows that immediately after irradiation, the shape and intensity of the EPR spectra of sucrose, fructose and glucose undergo changes during a certain period of time, characteristic for each material. The EPR spectrum, due to the remaining radical species, is then stable for a long time and can be used for dose estimations. Moreover, SS/EPR dosimeters may be archived for future measurements. Having this in mind, the EPR spectra of γ-irradiated saccharides were monitored from 5 min up to 5 months after the end of the irradiation (doses in the range 0.5–20 kGy). It was found that, although each saccharide dosimeter has its characteristic time evolution, they all reach a stable state.

The time evolution of the EPR spectra for arabinose, galactose and sorbose are shown in Figs. 2a–c respectively. The shape of the

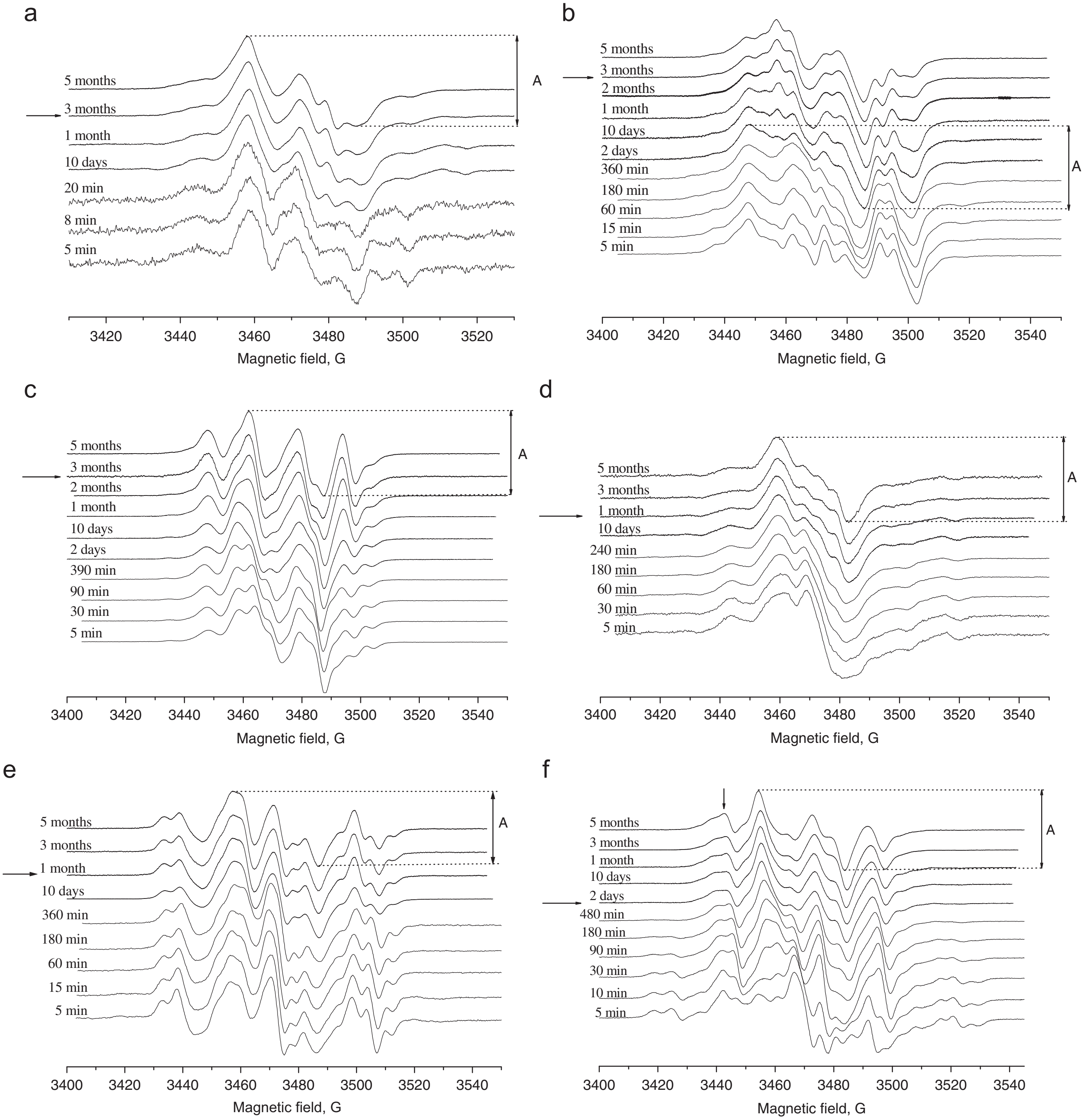


Fig. 2. Typical EPR spectra of irradiated saccharide powders recorded from 5 min to 5 months after irradiation: (a) arabinose; (b) galactose; (c) sorbose; (d) ribose; (e) trehalose; (f) lactose. With horizontal broken lines are marked intensities of the main peak of each sample used further in Fig. 2.

EPR spectra undergoes noticeable changes up to 3 months after irradiation, after which it is stable. In the case of ribose and trehalose (Figs. 2d and e), the EPR spectrum undergoes transformations in the first month after irradiation and then remains stable. The EPR spectrum of lactose (Fig. 2f) becomes stable after only 2 days, although there is a continuous small change in the low field part of the spectrum (indicated by the arrow) up to 1 month after irradiation. No further changes affecting the amplitude A indicated in Fig. 2 were recorded in the shape of the spectrum in the next 4 months of monitoring.

These results suggest that, with respect to time stability of the EPR spectra and the corresponding radiation-induced radicals, the disaccharides (trehalose, lactose) and ribose are more suitable for dosimetric purposes than the other monosaccharides (arabinose, galactose, and sorbose). However, comparing with earlier work, sucrose shows the best results in comparison with all saccharides studied up to now. Its spectrum becomes stable two days after irradiation and it was reported that almost the same EPR intensity was obtained after keeping the sample in a closed EPR tube for one year (Nakagawa and Sato, 2004).

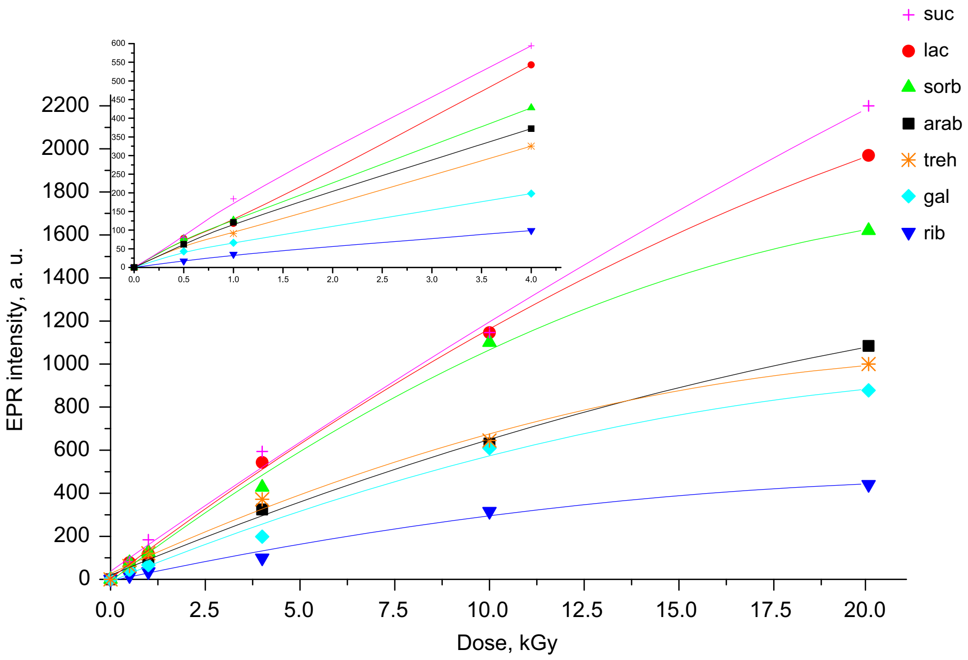


Fig. 3. EPR response as a function of the absorbed high-energy radiation dose estimated for all saccharides investigated in the present work, 3 months after irradiation.

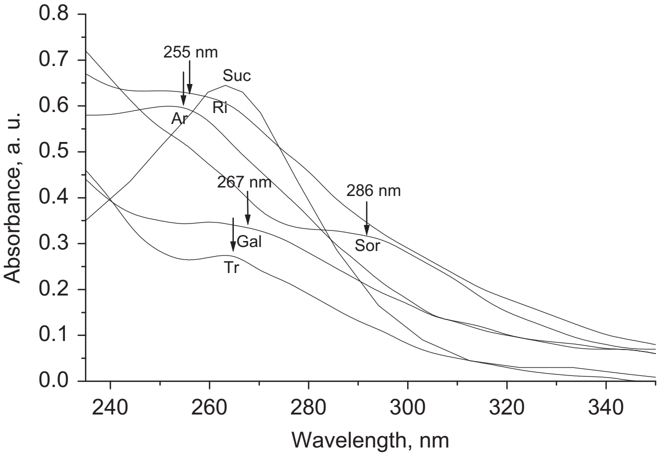


Fig. 4. UV absorption spectra of aqueous solutions of irradiated saccharide powders.

The dependence of the EPR signal intensity on the absorbed high-energy radiation dose, measured for all samples 3 months after irradiation, is shown in Fig. 3. The signal height A used to monitor the intensity is indicated on the spectra in Fig. 2. As the dose response was determined for samples of equal weight, the intrinsic radiation sensitivities of the different saccharides can be compared. Fig. 3 gives the following order of decreasing radiation sensitivity:
lactose > sorbose > arabinose > trehalose > galactose > ribose. As can be seen in Fig. 3, the EPR response of sucrose shows the best results in view of sensitivity. In view of a linear dose response, galactose and ribose dosimeters have linearity up to nearly 10 kGy whereas for arabinose, trehalose, lactose and sorbose linearity can be found up to about 4 kGy. In comparison with these saccharides sucrose as well as galactose and ribose shows a linear dose response up to 10 kGy. Basically the dependence EPR intensity vs. dose saturates at higher doses for all saccharides.

3.2. *UV absorption measurements on aqueous solutions of γ-irradiated saccharide powders*

Our previous investigation (Yordanov and Karakirova, 2007a) on sucrose as a potential dosimetric material has shown that the UV spectrum of aqueous solution of γ-irradiated sucrose powder exhibits an absorption band at 267 nm, which is not observed in case of a non-irradiated material. The same UV absorption band was recorded in gamma-irradiated single-crystal samples of sugar (Flores et al., 2000). This UV absorption band was attributed to a products of the radiation-induced radicals, formed in the solid and still present after dissolution in water. The presence of carbonyl groups in gamma-irradiated sugar was suggested by several authors (Flores et al., 2000; Khenokh, 1955). This hypothesis was recently supported by other authors (De Cooman et al., 2008, 2009). A linear dependence was found between the intensity of the UV band and the absorbed dose of high-energy radiation in sucrose (Yordanov and Karakirova, 2007a). This opened a new possibility of using UV spectrometry in the field of sugar dosimetry. In view of these findings, the present investigation was extended to UV spectrometric studies on aqueous solutions of γ-irradiated solid samples of mono- and disaccharides.

The UV spectra of aqueous solutions of equal wt % for all the saccharides were recorded in the region 240–350 nm, 3 days after γ-irradiation to 20 kGy and immediately after dissolution (Fig. 4).

It was found that for arabinose and ribose the absorption band is observed near 255 nm, for trehalose and galactose at 267 nm as for sucrose (Yordanov et al., 2002; Yordanov and Georgieva, 2004; Yordanov and Karakirova, 2007a), whereas for sorbose the maximum of the absorption band appears at 286 nm. In the case of lactose, a weak UV absorption band is present in the region 250–280 nm, but it is only poorly resolved. Lactose is therefore not suitable for UV dosimetry.

The time evolution of the UV absorption band intensity of the aqueous solutions of γ-irradiated saccharides was investigated during the first 12 days after dissolution, immediately after irradiation (Fig. 5). In between the measurements, the solutions were kept in closed vessels, in the dark and at RT. As seen in Fig. 5,

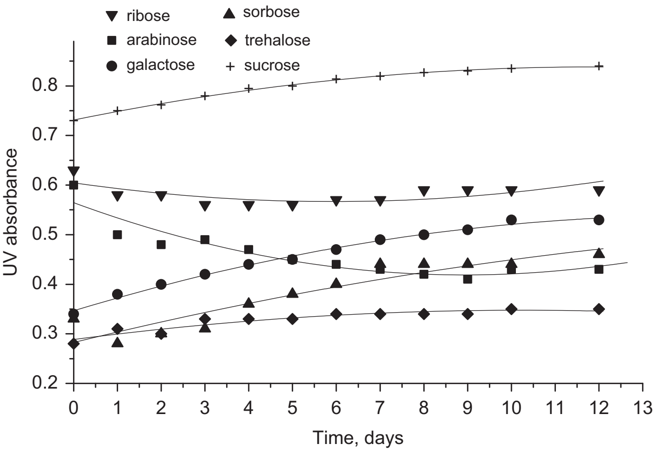


Fig. 5. The time evolution of the absorption intensity of the UV spectra recorded on aqueous solutions of irradiated saccharide powders.

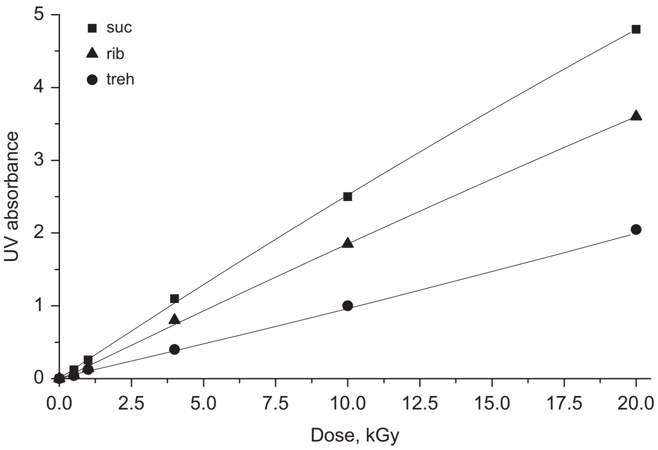


Fig. 6. The dependence of the UV absorbance on the absorbed γ-dose for all studied saccharides, after heating at 70 °C.

an increase of 15% is observed during the first 3 days for trehalose, after which a stable value is reached. Galactose and sorbose show increases of ca. 30% in the first ten days, and the data suggest that the signal has not stabilized yet after twelve days. For arabinose the opposite behavior is found - a decrease of approximately 30% within the first 10 days after dissolution, after which the signal seems to have stabilized. For ribose the UV absorption signal stabilizes faster (4 days) and is more radiation-sensitive than for the other saccharides (except sucrose). The present results show that arabinose, galactose and sorbose are not suitable as UV dosimetric materials, whereas ribose (and sucrose) seems to be best choice for this purpose. It should be noted, however, that in the case of ribose, the absorption maximum is not very well pronounced (Fig. 4). Everything considered, sucrose thus emerges as the best overall candidate for UV spectrometric dosimetry. However, stable UV absorbance is reached considerably faster in trehalose than in sucrose (where it takes 15 days after dissolution). In a previous study, it was shown that heating the aqueous solution of irradiated sucrose powder for 1 h at 70 °C was also sufficient to reach a stable state (Yordanov and Karakirova, 2007a). For this reason the aqueous solutions of irradiated trehalose and ribose were similarly heated and their UV absorbance as a function of dose was compared with that of sucrose. As can be seen in Fig. 6, ribose, trehalose and sucrose show a linear dose response up to 20 kGy when UV-absorvance monitoring is used. Because of its high sensitivity in comparison with the other saccharides sucrose remains the best candidate for UV spectrometric dosimetry.

4. Conclusions

The evolution of the EPR spectra of mono- and disaccharide powders was investigated for a period of 5 months after γ-irradiation. It is found that the shape of the EPR spectrum is stabilized after one month for ribose, trehalose and lactose and after 3 months for galactose, sorbose and arabinose. The spectra are then stable at least up to 5 months after irradiation. With respect to radiation sensitivity as measured by EPR spectrometry the following order is found: lactose > sorbose > arabinose > trehalose > galactose > ribose. Considering the EPR spectrum shape stability, the disaccharides trehalose and lactose and the monosaccharide ribose are more suited for dosimetric purposes. In terms of EPR sensitivity, lactose is more suitable than the other investigated saccharides, but its sensitivity is lower than for sucrose. For all saccharides, EPR signal amplitude can be defined that has a linear dose response at low doses, but saturates at higher doses.

With respect to the UV absorption of their aqueous solutions, all γ-irradiated saccharides undergo changes within the first days or weeks after dissolution. For lactose no pronounced absorption maximum is found and is thus not suited in the context of UV spectrometric dosimetry. Sucrose still performs best in this respect.

Taking the stability of both the EPR and UV spectra into account, the disaccharides are more suited for dosimetric purposes than the monosaccharides investigated in the present work. Among all saccharides studied up to now, sucrose remains the best dosimetric material, for both EPR and UV spectrometry.

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References

De Cooman, H., Pauwels, E., Vrielinck, H., Sagstuen, E., Sagstuen, E., Callens, F., Waroquier, M., 2008. Identification and conformational study of stable radiation-induced defects in sucrose single crystals using density functional theory. Journal Physics Chemistry B 112, 7298–7307.

De Cooman, H., Pauwels, E., Vrielinck, H., Sagstuen, E., Van Doorslaer, S., Callens, F., Waroquier, M., 2009. ENDOR and HYSCORE analysis and DFT-assisted identification of the third major stable radical in sucrose single crystals X-irradiated at room temperature. Physical Chemistry Chemical Physics 11, 1105–1114.

Flores, C., Cabrera, E., Calderon, T., Munoz, E., Adem, E., Hernandez, J., Boldu, J., Ovalle, P., Murrieta, H., 2000. ESR and optical absorption studies of gamma- and electron-irradiation sugar crystals. Applied Radiation and Isotopes 52, 1229–1234.

Karakirova, Y., Lund, E., Yordanov, N.D., 2008. EPR and UV investigation of sucrose irradiated with nitrogen ions and gamma rays. Radiation Measurements 43, 1337–1342.

Khenokh, M., 1955. Action of the rays from ^{60}Co on the carbohydrates. Dokl. Akad. Nauk SSSR 104 (5), 746–749.

Nakagawa, K., Nishio, T., 2000. Electron paramagnetic resonance investigation of sucrose irradiated with heavy Ions. Radiation Research 153, 835–839.

Nakagawa, K., Sato, Y., 2004. ESR investigation of sucrose radicals produced by particle irradiation. Spectrochimica Acta Part A 60, 1315–1318.

Nakagawa, K., Sato, Y., 2005. Investigation of heavy-ion-induced sucrose radicals by electron paramagnetic resonance. Radiation Research 164, 336–338.

Nakagawa, K., 2000. Effect of heavy irradiation on sucrose. Chemistry Letters vol. 29 (4), 422–423.

Nakagawa, K., Sato, Y., 2002. Effects of heavy ion irradiation on sucrose: an implication of ESR dosimeter for cosmic rays. Advances in ESR Applications 18, 253–257.

Nakajima, T., Otsuki, T., 1990. Dosimetry for radiation emergencies: radiation-induced free radicals in sugar of various countries and the effect of pulverizing on the ESR Signal. Applied Radiation Isotopes 41 (4), 359–365.

Nakajima, T., 1988. Sugar as an emergency populace dosimeter for radiation accidents. Health Physics 55 (6), 951–955.

Trivedi, A., Greenstock, C.L., 1993. Use of sugars and hair for ESR emergency dosimetry. Appl. Radiation Isotopes 44, 85–90.

Yordanov, N., Gancheva, V., Georgieva, E., 2002. EPR and UV spectroscopic study of table sugar as a high-dose dosimeter. Radiation Physics and Chemistry 65, 269–276.

Yordanov, N., Georgieva, E., 2004. EPR and UV spectral study of gamma-irradiated white and burned sugar, fructose and glucose. Spectrochimica Acta Part A 60, 1307–1314.

Yordanov, N., Karakirova, Y., 2007a. Sugar/UV spectrophotometric system for high-energy dosimetry (0.055–160 kGy). Radiation Measurements 42, 121–122.

Yordanov, N., Karakirova, Y., 2007b. EPR of gamma irradiated solid sucrose and UV spectra of its solution. An attempt for calibration of SS/EPR dosimetry. Radiation Measurements 42, 347–351.