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A comparative study based on dosimetric properties of different sugars

Z.M. Da Costa[a,b,*], W.M. Pontuschka[a], L.L. Campos[b]

[a]*Instituto de Física da Universidade de São Paulo/IFUSP, Departamento de Física Geral-Ala I Cidade Universitária, R. do Matão, Travessa R, No.187- 05508-900 São Paulo, Brazil*

[b]*Instituto de Pesquisas Energéticas e Nucleares, Calibration and Dosimetry Division, Cidade Universitária, Rua do Matão, Travessa R, No. 187- 05508-900 São Paulo, Brazil*

Abstract

Measurements of free radical densities in sugar by electron spin resonance (ESR) constitute a useful method for determining the dose received in the case of accidental irradiation because this material retains its radiation history. The aim of this work is to establish methods for practical dose assessment of people involved in ionising irradiation accidents, using two types of sugar: sucrose and dextrose. In this regard, practical considerations of sample preparation, grain size, ESR spectrum and spurious mechanical-induced ESR signal are discussed. Also presented are results for signal reproducibility, radiation response, signal stability and low-dose values. Studies on irradiated samples were carried out to explain the complex spectra derived from different paramagnetic species.

Keywords: ESR dosimetry; Sugar; Accident

1. Introduction

Ionising radiation produces a population of unpaired spins on lattice defects, radicals and changes the oxidation state of impurity ions. Some of the paramagnetic centres are stable with time and are measurable by electron spin resonance (ESR). ESR spectroscopy has been used in numerous dosimetry applications besides its powerful application as a research tool for the study of radiation related effects and materials characterisation (Ikeya, 1993).

ESR is a non-destructive technique for assessing quantities and characteristics of paramagnetic centres in a variety of materials. The method consists in the application of physical principles based on the number of unpaired spins created on irradiation.

ESR spectroscopy is currently employed in retrospective dosimetry. Retrospective assessment of the radiation dose is of fundamental importance to the analysis of the radiation risk and is an essential part of many related studies (Nakajima and Watanabe, 1974). Several materials are suitable for the retrospective dosimetry and can also be retrieved from accident sites. Among these, two types of sugar were chosen: sucrose and dextrose, aiming to standardise the sample preparation method and measurement conditions. The present technique is intended for

*Corresponding author. Instituto de Física da Universidade de São Paulo/IFUSP, Departamento de Física Geral-Ala I Cidade Universitária, R. do Matão, Travessa R, No.187-05508-900 São Paulo, Brazil. Fax: +55-3813-4334.

E-mail addresses: zamada@if.usp.br (Z.M.D. Costa), pontuska@if.usp.br (W.M. Pontuschka), lcrodri@net.ipen.br (L.L. Campos).

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practical applications in the field of accident personal dosimetry.

Recently it has been reported that sugar is one of the best dosimetric material for use in emergency dosimetry (Azorin et al., 1989; D'Errico et al., 1996; Generalova et al., 1993; Gutierrez and Azorin, 1993; Haldar et al., 1997; Nakajima, 1988; Trivedi and Greenstock, 1993; Tchen et al., 1993; Wieser et al, 1994). Furthermore, sugar is also a tissue equivalent material (effective atomic number = 6.92), relatively easily found at accident sites, provides a stable and dose dependent signal which is linear over a wide dose range, has low background signal before irradiation, and is widely used as a sample of easy preparation, without the need of any preliminary treatment (Kai et al., 1990; Nakajima et al., 1990; Nakajima, 1988, 1989, 1994, 1995; Gutierrez and Azorin, 1993).

Glucose, a simple monosaccharide sugar, is one of the most important carbohydrates used as a source of energy in animals and plants, and also in the pharmaceutical and food industries. Glucose ($C_6H_{12}O_6$) is a monosaccharide containing six carbon atoms. Five of the carbons plus an oxygen atom form a loop called "*pyranose ring*", the most stable form for six-carbon aldoses. In this ring, each carbon is linked to hydroxyl and hydrogen side groups with the exception of the 5th atom, which links to 6th carbon atom outside the ring, forming a CH_2OH group.

The ring structure may form in two different ways, yielding α glucose and β glucose. Structurally, they differ in the orientation of the hydroxyl group linked to the first carbon in the ring.

The natural form (D-glucose) is also referred to as dextrose (furan 6-C ring shown in Fig. 1) especially in the food industry. The older name of dextrose arose because a solution of D-glucose rotates polarised light towards the right. In the same vein D-fructose was called "levulose" because a solution of levulose rotates polarised light to the left.

Sucrose, $C_{12}H_{22}O_{11}$, consists of the dimmer glucose-fructose (Box et al., 1990; Budzinski et al., 1979; Flores et al., 2000; Sagstuen et al., 1986), linked by one oxygen atom, which constitute the glucosidic binding between the hydroxyl group (-OH) of the a sugar and the carbon of carbonyl radical (O=Ċ–H):

$$1\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow 1\underset{\text{glucose}}{C_6H_{12}O_6} + 1\underset{\text{fructose}}{C_6H_{12}O_6}\,.$$

The glucosidic binding involves the carbon 1 of the ring form of the glucose and the carbon 2 of the ring form of the fructose. Considering the existence of α and

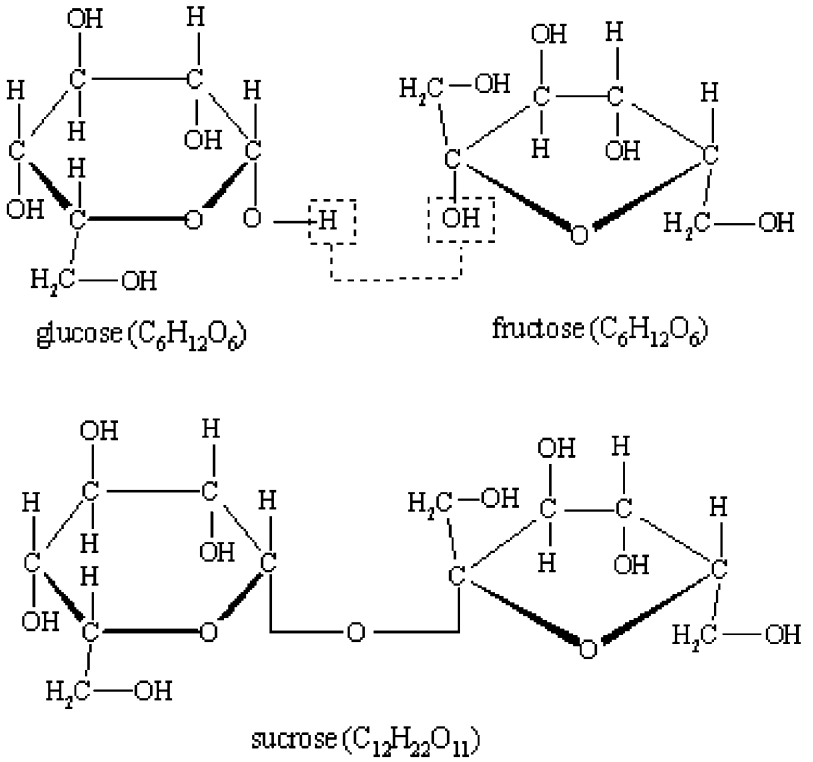

Fig. 1. Structural formula of the sucrose (glucose + fructose).

Table 1
Typical settings of ESR spectrometer parameters for measurement of sugar

Magnetic field parameters	Microwave parameters	Signal channel parameters
Centre field: ca. 350 mT	Microwave frequency: Ca. 9.8 GHz	Modulation frequency: 100 KHz
Sweep width: 2–10 mT	Microwave power: 1–40 mW	Modulation amplitude: 0.1–5 mT
Time of sweep: Variable		Conversion time: 20 ms
Resolution: 4096 points		Time constant: 80 ms
		Number of scans: 1–100

β forms of glucose and fructose, it implies that sucrose consists of mixed isomers (Fig. 1).

Among a variety of mono- and disaccharides we observe that the samples of sucrose and dextrose exhibit the most sensitive responses in agreement with the other authors (Trivedi and Greenstock, 1993). For this reason we chose these sugars for all subsequent studies.

2. Material and methods

In this work two types of sugar were selected and studied: common sugar cane and dextrose not yet completely characterised for dosimetry purposes, in the form of white amorphous powder, purchased from a local market (purity of these sugars is approximately 98–99%). The samples were used without preliminary treatment because ESR results have shown a low background signal before irradiation.

The mechanical effect of crushing the sugar on the ESR signal was evaluated. Some samples were crushed manually yielding a powder with different grain sizes. The choice of the optimal grain size considers the anisotropy of the dosimetric signal and the influence of the preparation method on the induced signal. The goal is to achieve the highest possible measurement precision for the dosimetric signal amplitude (Nakajima et al., 1990).

All the samples were irradiated with ^{60}Co-gamma radiation, at room temperature, under electronic equilibrium conditions and placed in fused silica ESR sample tubes. The dosimetric calibrations were carried out in the radiation fields of the Radiation Technology Centre—CTR of IPEN. After sample preparation, storage temperature and humidity could influence the response because microwaves are strongly absorbed by water content. Therefore, the samples were stored in controlled environment with low relative humidity, aiming to eliminate spurious temporary signals.

The ESR measurements were performed using a conventional X band spectrometer Bruker-EMX (Bruker Instruments, Billerica, MA) with a standard rectangular cavity (model ER 4102 ST) of the Physics Institute, University of São Paulo. The measurements' parameters are shown in Table 1.

The first derivative of absorption spectrum is displayed and the peak-to-peak amplitude values of the signal are recorded for relative dose measurements and are based on linear dose dependence. The assessment of the absorbed dose can be done by the additive method or by the dose response curve (IAEA-TECDOC-1331, 2002). This work used the dose response curve method for dose reconstruction since it is a non-destructive fast method and the variation of radiation sensitivity of sugar is independent of the applied dose evaluation method. The parameters of the calibration curve, slope and interception with dose axis were determined by linear regression analysis.

The sugar was produced and purified by different manufactures in Brazil, and the possibility of the inclusion of eventual impurities was considered. Such impurities may introduce extraneous free radicals, often difficult to be accurately evaluated. The typical results were obtained based on semi-quantitative analysis for sucrose using emission spectrographic method, as shown in Table 2. For this reason, the best commercial products available in the market were used and samples containing impurities were discarded.

3. Results

As shown in Fig. 2 (curve A1 or amplified in curve A2) the non-irradiated powdered sucrose exhibits a very broad and weak ESR signal (Flores et al., 2000; Wieser

Table 2
Semi-quantitative analyses for sucrose using emission spectrography

Element	Average concentration (%)
B	0.003
P	0.15
Fe	0.0075
Cr	0.0045
Ni	0.0045
Zn	0.15
Si	0.006
Al	0.006
Mn	0.0015
Mg	0.0045
Pb	0.0045
Sn	0.003
Bi	0.0015
V	0.003
Cu	0.0045
Ba	0.015
Co	0.0045
Ca	0.0075
Sb	0.0045

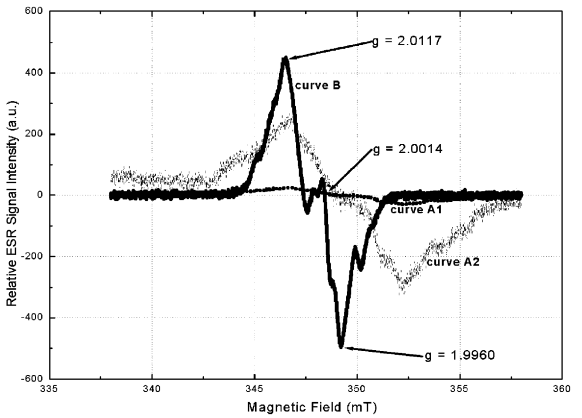

Fig. 2. Curve A1—First derivative of the absorption curve (arbitrary units) of unirradiated sucrose with respect to the applied magnetic field (mT). Curve A2—Amplified first derivative of the absorption curve (arbitrary units) of unirradiated sucrose with respect to the applied magnetic field (mT). Curve B—First derivative of the absorption curve (arbitrary units) of sucrose with respect to the applied magnetic field (mT) irradiated with ^{60}Co gamma rays. The g values of the independent spectral components are shown.

et al., 1994), which could only be detected using signal accumulation. It appears near the magnetic field setting of the irradiated samples and these spectra are similar. Unirradiated dextrose exhibits a relatively weak ESR signal (not shown).

The results suggest that ESR signal from free radicals found in the powdered sugar with grain size $<80\,\mu m$ non-irradiated are similar to those in irradiated one and the relative ESR absorption intensity increases as the powder size decreases, due to mechanical manipulation (Nakajima et al., 1990, 1995; Fattibene et al., 1996; Wieser et al., 1994). Other authors also point out this problem of a possible overestimation in the low-dose range (Nakajima and Otsuki, 1990).

Fig. 2 (Curve B) shows the typical powder spectrum obtained for sucrose samples after gamma irradiation, and consists of a single line centred at $g=2.0014$ and having a structure of equally spaced weak resonance. Different types of ionising radiation produce essentially the same ESR signal. It is not possible to distinguish the radiation type of radiation-induced radicals. Similar ESR spectra were obtained from different sugar samples found in Brazil, where the g-factor also does not change.

The spectrum is complex, likely derived from more than one radical and corresponds to an average of all possible crystal orientation (Fattibene et al., 1996).

From the structural formula showed in Fig. 1, it was obvious that glucose had a lot of hydroxyl groups. Given that the molecular size of glucose is relatively small and the molecule is flexible, it could be an excellent donor for hydrogen bonding.

When the samples of sucrose are irradiated, free radicals are formed as radiolysis products. The exact nature of the electron trapping is yet unknown, but some conclusions are possible. In our opinion, the complex behaviour might be the result of super hyperfine interactions.

Flores (Flores et al., 2000) using sucrose crystals showed that the ESR transitions are the same as those observed in powder spectrum and interpreted them as hyperfine structure due to the interaction of an unpaired electron spin produced during the irradiation process with eight equivalent nuclear spins of 1/2 contained in the structure of the sucrose molecule, which are attributed to the neighbouring hydrogen atoms.

Other works based on ENDOR (electron nuclear double resonance) and EI-ESR (ENDOR-induced ESR) point out the spectrum structure in terms of one α and two equivalent β-protons and predicted at least six components contributing to the total ESR spectrum of irradiated sucrose (Vanhaelewyn et al., 2000).

One comparative study was performed using the dextrose and the results obtained are shown in Fig. 3, where it is possible to observe some differences, but probably they are derived from the some radicals present in the sucrose. A more extensive study of this system using other techniques is required.

This work studied the number of free radicals as a function of the applied ^{60}Co gamma radiation dose to obtain a calibration curve for dosimetric purposes. The dose-response curve for sucrose samples and dextrose

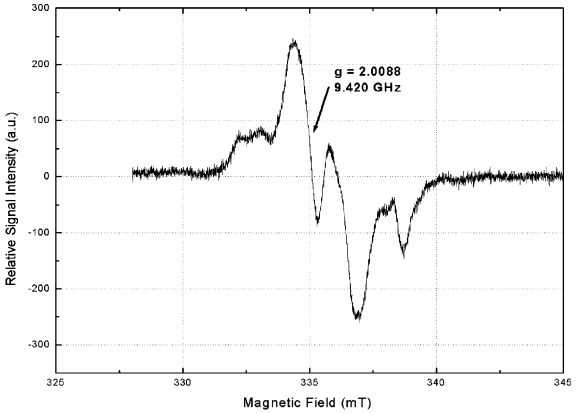

Fig. 3. First derivative of the absorption curve (arbitrary units) of dextrose with respect to the applied magnetic field (mT) irradiated with ^{60}Co gamma rays. The g value of the independent spectral components is indicated.

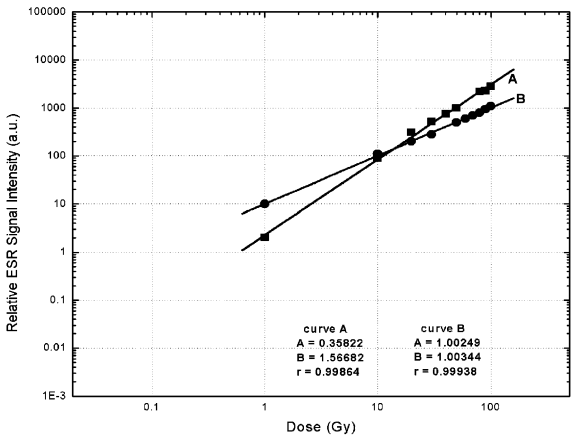

Fig. 4. Curve A—Dose response curve of sucrose irradiated with ^{60}Co gamma rays at room temperature. Curve B—Dose response curve of dextrose irradiated with ^{60}Co gamma rays at room temperature.

samples irradiated with gamma doses between 1 and 100 Gy are shown in Fig. 4 (Curve A- sucrose and Curve B- dextrose).

It can be observed that sucrose is more sensitive than dextrose, but for both sugars the free radical ESR signal increases linearly with the radiation dose over a wide range (0.1–100 Gy). The minimum detectable dose is 0.1 Gy.

The influence of post-irradiation storage on the radiation ESR response of the sucrose and dextrose was investigated. The samples were measured immediately after irradiation at room temperature and subsequently measured each hour for one week. The post-irradiation fading resulted is, not significant 2–3% decay of the signal amplitude over one week, but the intensity of the signal increased very slightly within the first days (Nakajima, 1989). Therefore, all measurements were performed more than 24 h after the irradiation, to eliminate spurious temporary signals.

4. Conclusion

In this work, we have undertaken to obtain some information that could contribute to the development of a method for estimating the absorbed dose received in a radiation accident. It was proposed to use ESR measurements of the free radicals generated by irradiation in two selected types of sugar: sucrose and dextrose. These saccharides are easily available, cheap and also tissue-equivalent and should serve as a good alternative to other materials in industrial emergency and medical dosimetry.

The results of this study can be summarised as follows:

- The dextrose (D-glucose) widely used in pharmaceutical industry and analysed by ESR can serve as an effective radiation monitoring material, mainly in retrospective dosimetry;
- Sample grinding presents some disadvantages: an increase in background signal, generation of stable signals, and dependence of the sensitivity to ionising radiation on grain size. The findings indicate the possibility of dose overestimation when small grains are used and average grain size of 80–200 μm is recommended;
- No effects of impurity elements contributing to the ESR signal were found in any sugar produced in Brazil, indicating that any sugar sample is suitable for accident dose assessment.
- The similarly showed by structural formula and spectra of the sucrose and of the dextrose open new possibilities of study.

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