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Mannitol as a radiation sensitive material for electron paramagnetic resonance dosimetry

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The possibility of solid state/mannitol ($C_6H_8(OH)_6$) dosimeters as a radiation sensitive material for γ-ray irradiation using electron paramagnetic resonance (EPR) spectroscopy, is reported. The peak-to-peak signal amplitude of the first derivative of the EPR spectrum is used as a dosimetric index. The influence of some EPR parameters, such as the microwave power and modulation amplitude on the peak-to-peak height of the EPR spectra of the irradiated mannitol is studied. The dose response curves for γ irradiated mannitol in two dose ranges (1-20 Gy and 0.5-20kGy) are investigated. It was found that mannitol can be considered as a useful radiation sensitive material in the ranges of 1-20 Gy and 0.5-10 kGy. Sucrose is used for comparison and reference.

Keywords: EPR spectroscopy, irradiation, mannitol, free radicals

INTRODUCTION

Ionizing radiation generates stable free radicals in some materials. For quantitative determination of the radiation-induced free radicals, several methods are used. One of the most popular in this area is the electron paramagnetic resonance (EPR) spectroscopy. The problem for the determination of the absorbed dose of ionizing radiation using solid state/EPR dosimetry has attracted the attention of researchers for about 50 years. The advantages of these dosimeters are: simple and rapid dose evaluation, non-destructive analysis permitting repeated measurements and thus allowing storage for archival purposes.

In the last two decades the alanine-EPR dosimetric system was recognized by the International Atomic Energy Agency (1-3) as a routine, reference and transfer dosimeter for industrial irradiators operating in the kGy range of doses. The radiation sensitivity of alanine is comparatively low and this has prompted the search for alternative materials. In order to increase the sensitivity of the solid state/EPR dosimetric system, up to now several materials as: sucrose (4-8), lithium lactate (9), aspartame (10, 11), xylitol and sorbitol (12,13) have been studied as dosimetric materials. It is well known that ionizing radiation generates stable long-lived free radicals in some saccharides. Recent study shows that among several mono- and disaccharides, sucrose shows the best dosimetric properties (14). Despite good dosimetric characteristics of alanine and sucrose, the investigators continued to look for others materials, which can be used as dosimeters.

In view of the importance of the problem, mannitol was studied as a possible dosimetric material.

The aim of the present work is to investigate the possibility for estimation of the absorbed dose gamma rays using mannitol/EPR dosimeters. Because of the complex EPR spectrum obtained after irradiation, the important step was to investigate the influence of some EPR spectrometers settings parameter. Mannitol investigated in this work has never before been considered for dosimetric purposes.

EXPERIMENTAL

Materials and preparation of the solid state/EPR dosimeters

Mannitol is a white, crystalline sugar alcohol with the chemical formula $C_6H_8(OH)_6$. It is used in analytical chemistry, medicine, foods and so on. In foods mannitol is used as a sweetener for people with diabetes, in mint candies, chewing gums and dried fruits.

Mannitol, used as a radiation sensitive material, was purchased from Aldrich and paraffin, used as a binding material, from Merck. Both of them were used as obtained.

The solid state/EPR dosimeters (SS/EPR) were prepared from a homogeneous mixture of mannitol (60 % w/w) and paraffin (40 % w/w) (15). Solid

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dosimeters were pressed in the form of cylinders with diameter 4 mm and length of 10 mm.

Irradiation

The dosimeters were irradiated with γ-rays on a "Gamma-1300" irradiator (^{137}Cs) with a dose rate of 200 Gy/h in two dose ranges - 1-20 Gy and 0.5–20 kGy. The irradiation procedure was performed in air at room temperature. After irradiation all samples were kept in closed plastic bags at room temperature and were stored in dark.

In order to avoid all interferences in dose estimations due to any short-living species and transition EPR spectra, all measurements were performed at least 72 h after irradiation.

Isothermal annealing of the free radicals in the dosimeters

After irradiation, part of the mannitol dosimeters were kept for several h at 50°C in a desiccator. EPR spectra were recorded every hour. The aim was to investigate the time dependence of the dosimeters at 50°C.

Instrumentation

The EPR spectra were recorded at room temperature on a JEOL JES-FA 100 EPR spectrometer operating in the X–band, equipped with a standard TE_{011} cylindrical resonator. The dosimeters were placed in quartz tubes and were fixed in the cavity center. The instrumental settings using the above spectrometer were: modulation frequency 100 kHz, magnetic field sweep 10 mT, time constant 0.3 s and sweep time 2 min. Other parameters as microwave power and amplitude of the magnetic field modulation were varied in order to find the most suitable value to record the maximal intensive and non-deformed EPR spectra.

RESULTS AND DISCUSSION

Features of the EPR spectrum of mannitol dosimeters

In a non-irradiated mannitol/EPR dosimeter, no EPR spectrum was recorded. After irradiation all dosimeters exhibited an EPR spectrum with g factor of 2.0170 ± 0.0002 of the most intense peak (Figure 1).

In the X-band it is unresolved and a complex signal contains several overlapped and not well resolved EPR patterns. The nature of these radicals is not cleared up to the moment.

It was found that the EPR spectrum of irradiated mannitol strongly depends on the applied microwave power and modulation amplitude. Because of that, the first step after irradiation was to study the influence of these instrumental settings. A set of EPR spectra at different magnitudes of the microwave power is given in Figure 2.

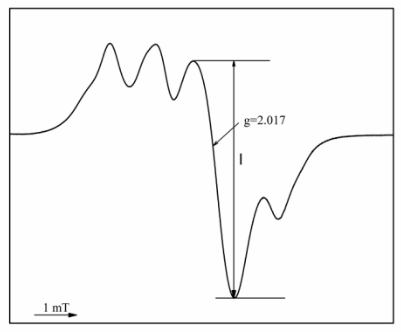

Fig. 1. EPR spectrum of γ irradiated mannitol EPR/dosimeter three days after irradiation with a dose of 10 kGy. The microwave power is 1 mW, modulation amplitude – 0.16 mT.

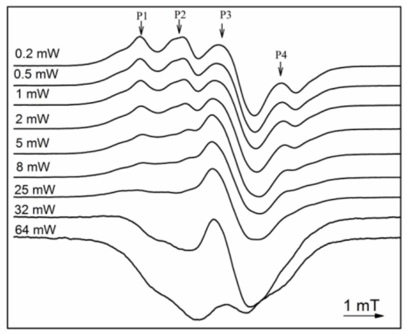

Fig. 2 A set of EPR spectra of γ irradiated mannitol at different microwave powers. Modulation amplitude is 0.05 mT.

It is seen from this figure that the EPR spectrum of the radiation-induced free radicals of mannitol has four peaks (noted as P1, P2, P3 and P4) and they are sensitive to the magnitude of the applied microwave power. It was found that the peaks P1, P2 and P4 have an equal behavior of saturation. They are saturated even at microwave power of ca. 0.2 mW. At a microwave power above 8 mW these peaks disappeared. Because of the same behavior of saturation from the applied microwave power we can conclude that the peaks P1, P2 and P4 are probably due to the one and the same radical. The peak P3 is slightly broadened at a microwave power higher than 1 mW, which unambiguously indicates a saturation effect. Figure 3 shows the dependence of EPR signal intensity as a function of the square root of microwave power.

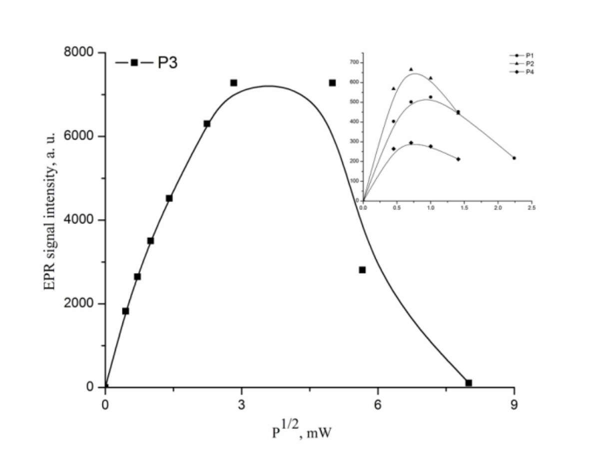

Fig. 3. The peak-to-peak signal intensity as a function of the square root of the applied microwave power. The modulation amplitude is 0.05 mT.

As can be seen, the peak-to-peak signal intensity of P3 strongly increases with the increase of the applied microwave power from 0.2 to 8 mW, reaching a maximum at ca. 25 mW, and decreases at higher microwave power values. At a microwave power of 64 mW the EPR signal reaches a minimum, which means that it is completely saturated. The peak-to-peak signal amplitude of the other peaks increase with microwave power to 0.2 mW and after that decrease because of saturation. In view of that, P3 was further used to study the EPR response of mannitol as a function of the absorbed dose ionizing radiation at a microwave power of 1 mW.

On the other hand, the EPR spectrum of irradiated mannitol depends on the applied modulation amplitude, as was mentioned before. Because of that, the dependence of the shape of the EPR signal to the applied modulation amplitude was studied. Figure 4 shows the dependence of peak-to-peak signal intensity as a function of applied modulation amplitude.

Linearity can be seen to about 0.16 mT; after that over-modulation of the separated EPR lines appears. In view of this, 0.16 mT modulation amplitude was chosen to examine the dose response of mannitol.

Time stability of radiation-induced EPR signals

From dosimetric point of view the time stability of radiation-induced EPR signals is an important feature for every EPR dosimeter. This is because solid state/EPR dosimeters have the advantage of being suitable for estimation of the absorbed dose high energy radiation not only immediately after irradiation but also to be archived for future measurements. Previous works [6, 14, 16] show that immediately after irradiation, the shape and the intensity of the EPR spectra of saccharides 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. The EPR spectrum of irradiated solid sucrose undergoes changes within 72 h after irradiation and then becomes stable [16]. Having this in mind, the EPR spectra of γ-irradiated mannitol were monitored from 3 days up to 3 months after the end of the irradiation (Figure 5).

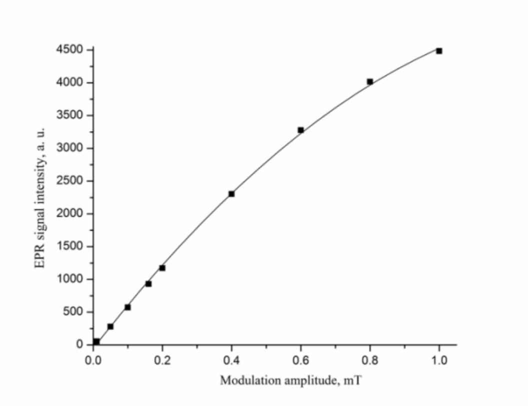

Fig. 4 The EPR signal intensity of γ irradiated mannitol as a function of applied modulation amplitude.

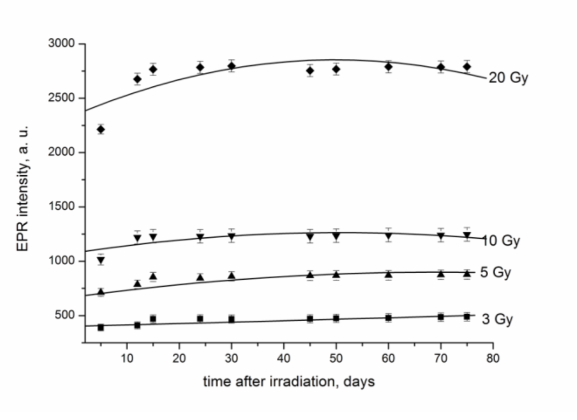

Fig. 5 Time stability of EPR signals intensity

The EPR spectra undergo small transformations in the first days after irradiation. It was found that the peak-to-peak signal intensity and the width of the signal noted as P3 in the EPR spectrum (Figure 2) have changed. As can be seen from Figure 5, the peak-to-peak signal intensity of irradiated mannitol increased with about 25 %. The above results show that in mannitol some processes take place during the irradiated and in the first days after irradiation, which lead to broadening of the lines and increasing of the peak-to-peak signal amplitude. These changes could be due to the influence from more short-lived species fading out during the first 10 days and saturated at a lower microwave power. After 10 days, the line width and the peak-to-peak amplitude became stable. In order to shorten the period to reach a stable EPR spectrum (in view of line width and peak-to-peak amplitude) immediately after irradiation the irradiated samples were kept at 50°C for several h. An EPR spectrum was recorded every h. It was found that heating for 5 h at 50°C is enough to stabilize the EPR spectrum of γ irradiated mannitol. Following this procedure it is not necessary to wait 10 days before starting dosimetric measurements.

EPR response of mannitol to radiation dose

For a dosimeter a linear dose response is required for relative dose measurements, but most dosimeters show such a good behaviour only within a certain dose range. The dependence of the EPR signal intensity of γ irradiated mannitol on the absorbed dose of ionizing radiation in two dose ranges 1-20 Gy and 0.5-20 kGy was investigated (Figure 6).

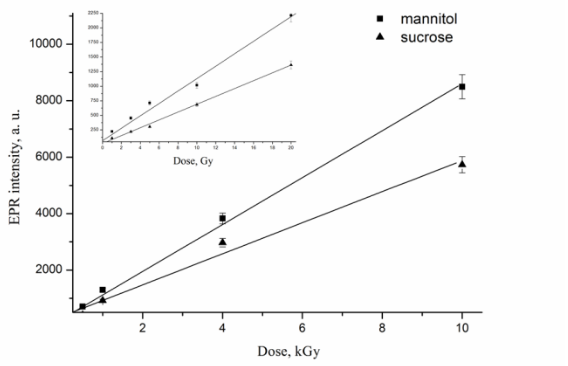

Fig. 6. The dependence of the EPR signal intensity of γ irradiated mannitol and sucrose on the absorbed dose ionizing radiation in two dose ranges: 1 - 20 Gy and 0.5 - 10 kGy.

In the sample irradiated with 1 Gy of γ rays the contribution of the noise to the signal is very large and it is necessary to make more than 35 accumulations to reach S/N ≥ 2. For samples irradiated with 3 Gy the EPR measurement was repeated 10 times to improve the signal-to-noise ratio. In case of 10 accumulations, the ratio S/N is equal to 2. In view of this, the detection limit was obtained as 1 Gy. It is possible to reach even lower doses, but then more than 100 accumulations should be done. Mannitol shows a linear dose response for doses of 1 to 20 Gy, and from 0.5 to 10 kGy with saturation at higher doses. In comparison with mannitol, sucrose shows a linear dependence of the EPR signal intensity of the absorbed dose ionizing radiation in the investigated dose range (to 20 kGy). In view of radiation sensitivity, mannitol shows good results comparable with these of sucrose, but it can be used for doses up to 10 kGy.

CONCLUSIONS

Mannitol is a useful dosimetric material for dose ranges of 1 – 20 Gy and 0.5 – 10 kGy. It has the disadvantage that a few days are needed before the assumed unstable short-lived radicals have decayed. This disadvantage can be eliminated with the proposed procedure of isothermal annealing.

On the basis of the microwave power saturation it was found that at least two different radicals are present in the γ irradiated mannitol.

The present studies on the properties of mannitol as a radiation sensitive material show its suitability as an alternative to sucrose, but with some limitations:

- the detection limit is about 1 Gy, whereas it is about 0.5 Gy for sucrose;
- the maximal dose of radiation that can be measured is up to 10 kGy, whereas it is 20 kGy for sucrose.

The obtained results show that mannitol is a promising dosimetric material, but there is still work to be done before it can be taken in routine use as a dosimeter.

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МАНИТОЛ КАТО РАДИАЦИОННО ЧУВСТВИТЕЛЕН МАТЕРИАЛ ЗА ДОЗИМЕТРИЯ С ЕЛЕКТРОН ПАРАМАГНИТЕН РЕЗОНАНС

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(Резюме)

Представена е възможността за използване на твърдо тяло/дозиметри, съдържащи манитол, като радиационно чувствителен материал за гама облъчване, с помощта на електрон парамагнитен резонанс спектроскопията. Като дозиметричен индекс е използвана амплитудата на сигнала от пик до пик на първата производна на ЕПР спектъра. Изследвано е влиянието на апаратурните ЕПР параметри, мощност на микровълновото лъчение и амплитуда на модулация, върху интензитета на ЕПР сигнала на облъчен манитол. Изследван е дозовия отклик на гама облъчен манитол в две области от дози (1 – 20 Gy и 0.5 – 10 kGy). Установено е, че манитолът може да бъде полезен радиационно чувствителен материал в областта от 1 до 20 Gy и от 0.5 до 10 kGy. Като референтен материал е използвана захароза.