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EFFECT OF TEMPERATURE ON THE EPR RESPONSE OF GAMMA IRRADIATED POTASSIUM TARTRATE HEMIHYDRATE

(Kesan Suhu Terhadap Kalsium Tartrate Hemihidrat yang Didedahkan Kepada Sinar Gama Menggunakan Spektrometer Resonan Elektron Paramagnet)

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Abstract

Electron paramagnetic resonance (EPR) can be used as radiation detection for appropriate materials exposed to ionizing radiation. In this study, potassium tartrate hemihydrate (PT) was irradiated with Co-60 gamma rays with absorbed dose range from 1 to 9 Gy. The effect of temperature to the unirradiated and irradiated samples were investigated using electron paramagnetic resonance (EPR) spectroscopy. The EPR spectra were recorded in the temperature range from room temperature (293 K) to 413 K. The results show that the unirradiated PT sample does not exhibit any EPR signal when thermal energy is given to the sample. However, the irradiated PT samples exhibit EPR spectrum with three lines recorded at room and high temperatures. The main strong line dominates the spectrum of the irradiated PT sample appears at g = 2.0032. Heating the irradiated sample above room temperature showed increases in signal intensity. The dose response curves of the signal at variable temperature were described well by a linear function.

Keywords: potassium tartrate hemihydrate; EPR dosimetry; gamma radiation

Abstrak

Kaedah resonan elektron paramagnet (EPR) boleh digunakan sebagai kaedah pengesanan sinaran menggunakan bahan tertentu yang didedahkan kepada sinaran mengion. Di dalam kajian ini, sampel kajian iaitu kalsium tartrate hemihidrat diuji sebagai bahan untuk pengesanan sinaran. Ia didedahkan kepada sinar gama dari sumber kobalt-60 dengan dos terserap antara 1 hingga 9 Gy. Kesan suhu terhadap sampel kajian yang tidak didedahkan dan juga yang didedahkan kepada sinar gama dikaji menggunakan spektroskopi resonan elektron paramagnet. Suhu kajian yang digunakan semasa merekod spektrum EPR ini adalah di dalam julat 293 K hingga 413 K. Keputusan kajian menunjukkan, sampel yg tidak didedahkan kepada sinar gama tidak merekodkan sebarang isyarat walaupun tenaga haba diberikan semasa merekod isyarat. Walaubagaimanapun, sampel yang didedahkan kepada sinar gama menunjukkan terbentuknya tiga isyarat spektrum EPR pada suhu bilik dan juga pada suhu yang tinggi. Isyarat kuat yang mendominasi spektrum sampel yang didedahkan kepada sinaran berlaku pada nilai faktor g = 2.0032. Apabila suhu untuk merekod isyarat EPR ditingkatkan daripada suhu bilik, keamatan isyarat bagi sampel yang didedahkan kepada sinaran juga meningkat. Lengkung sambutan dos terhadap isyarat EPR pada suhu yang berbeza dapat dijelaskan menggunakan fungsi linear.

Kata kunci: kalsium tartrate hemihidrat; dosimetri EPR; sinar gama

Introduction

A free radical is an atom, a group of atoms, or a molecule in a certain state containing one unpaired electron which occupies an outer orbital [1]. The formation of free radicals usually initiated by reactions such as thermal energy, light, gamma radiation, and mechanical forces. Electron spin resonance (ESR), also sometimes called electron paramagnetic resonance (EPR) spectroscopy can be used to detect the free radicals because an unpaired electron, and a free radical has magnetic properties due to the intrinsic angular momentum which known as electron spin. On dosimetry application, ESR spectroscopy has been used successfully based on the fact that the free radicals formed by irradiation of organic and inorganic solid substances. Alanine–EPR dosimetry for instances, is an accepted dosimetry system for high dose application, approve by the International Atomic Energy Agency (IAEA) as a secondary high dose standard and with a specific internationally approved procedure and instrument setting for measurements [2]. It is also suitable for a reference standard, transfer standard and routine dosimetry [3]. Although the successfulness of using alanine-EPR dosimetry in high radiation dose level, alanine is not suitable for clinical application where dose down to 0.5 Gy [2]. This has motivated researchers to explore a new sensitive EPR dosimetry material if alanine is inadequate or as an alternative to existing methods of dose measurement. In this regard, other dosimeter materials such as formates [4, 5], dithionates [6,7] and tartrates [8,9,10] have been evaluated in the literature. Strategy to find the new materials also was discussed by Ikeya et al. [11]. They proposed that a new material should have a large number of stable radical pairs per 100 eV radiation energy, sharp spectral lines and thermal stability of the radicals at room temperature.

The effect of temperature on the EPR dosimetry material is very important to take into account by the researchers who try to find new dosimetry materials. In the selection of the operating temperatures of the sample, one have to consider the temperature range in which prior work would lead to observe a spectrum of the sample. In this regard, the aim of the present work is to investigate the effect of temperature performed at room and high temperatures to irradiate and unirradiated potassium tartrate hemihydrate (PT). The behaviour of radiation induced radical of PT at different temperatures were investigated through the EPR spectra and EPR signal intensity. The dosimetric potential of PT in a lower dose range (1-9 Gy) is also investigated.

Materials and Methods

PT ($[CH(OH).COOK]_2.1/2H_2O$) samples were purchased from Fisher Scientific UK Ltd. with 99% purity and used without any further treatment. The samples were transferred to the polythene bag and exposed to ^{60}Co gamma rays at room temperature delivered by gamma ray from Eldorado 8 therapy unit at Secondary Standard Dosimetry Lab (SSDL), Nuclear Malaysia Agency. Solid water phantom (30 x 30 x 15 cm^3) was used during the exposure. It provides dose equivalent to that for water. The dose values were calculated using irradiation time and the dose rate (101 mGy min^{-1}). The dose rate at the sample site was measured using ionizing chamber NE 2571 #1028 and electrometer PTW-Unidos 10005 #50013. The source detector distance is at 80 cm and the beam field size was set to 25 x 25 cm^2. The samples were exposed from 1 up to 9 Gy.

After irradiation treatment of samples, PT samples were transferred into Suprasil® quartz EPR sample tubes with inner diameter of 4 mm. The samples were filled in the tubes with the height range about 5 – 7 mm from the bottom and its masses are in the range of 50 - 65 mg. EPR spectra were recorded in the temperature range from room temperature (293 K) to 413 K conducted in X-band microwave frequency with a JEOL JES-FA200 ESR spectrometer system equipped with TE011 cylindrical cavity. The sample temperature inside the microwave cavity was monitored with a digital temperature control unit (JEOL ES-DVT4). During the measurement, the tubes were closed with the Teflon® caps to prevent the sample from loss during temperature gradient. The filled sample tube was aligned at the center of the cavity using a sample tube length setting device, and holder together with sample tube fixture were used to preserve identical positions in the cavity.

The g-value of stable signal from the samples was calibrated using Mn^{2+} as a reference and the signal intensity is quantify by measuring the peak to peak values because this is the most reliable method [9]. The signal from reference sample, Mn^{2+} also recorded together with the analysed sample to secure the stability of the spectrometer during the signal study. The measurements were carried out at microwave frequency, ~9.2 GHz; microwave power, 1 mW; center field, 327 mT; sweep width, 10 mT; sweep time, 30 s; modulation frequency, 100 kHz; modulation width, (0.7 mT); amplitude, 300; time constant, 0.3 s and the number of accumulated scans, 3.

Results and Discussion

The Effects of Temperature on EPR Spectra of Unirradiated PT

Generation of free radical can be initiated by thermal energy itself. The EPR signal intensity recorded in an EPR spectrometer is directly proportional to the spin population in the lower state due to the Boltzmann factor, which varies inversely with the temperature [1]. In this respect, the unirradiated PT sample was investigated at different high temperature to observed whether thermal energy alone can produce free radical in PT sample or not. The result was given in Figure 1. Figure 1 shows the EPR spectra of unirradiated PT samples recorded in a temperature range of 293 – 393 K. The unirradiated PT sample does not show any EPR signal even though the temperature given to the sample is increased from room temperature to 393 K.

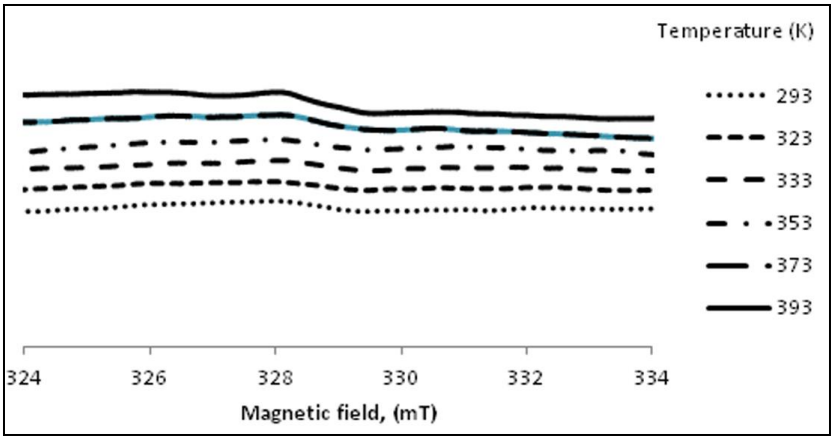

Figure 1. The EPR spectra of unirradiated PT at different temperature

The effects of temperature on EPR spectra, signal intensity and dose response curve of irradiated PT

Figure 2 (a) shows the EPR spectra of PT samples irradiated at a dose of 9 Gy recorded at different temperature. Meanwhile, Figure 2 (b) illustrated the EPR signal intensity of PT sample (I_2) irradiated at 1, 3, 7 and 9 Gy recorded at different temperature.

The irradiated PT samples exhibit EPR spectrum with three lines label as I_1, I_2 and I_3 as shown in Figure 2 (a) at room temperature and high temperature. One main strong line (I_2) dominant the spectrum appears at g = 2.0032 and has a peak-to-peak line width of ΔHpp = 1.0 mT. The g value of the I_2 was remained unchanged even recorded in the different temperatures. These results show that gamma radiation can generate radicals in PT samples, but the thermal energy source does not have enough energy to produce radicals responsible for resonance signals I_1, I_2 and I_3. By analysing the number of lines, line separation and relative intensity of irradiated PT sample, it is shown that, irradiated PT produce EPR spectra with hyperfine structure due to equivalent protons [1]. In this case, one unpaired electron interacts with two equivalent protons with hyperfine splitting about 2.4 mT. Hyperfine splitting is the separation between the two hyperfine lines of the spectrum express in magnetic field unit.

To observe the change occur in the irradiated spectra due to the temperature, the signal intensity of I_2 was analysed. The variation in signal intensities of I_2 recorded in a temperature range of 293 – 413 K were given in Figure 2 (b). The samples were irradiated to the dose of 1, 3, 7 and 9 Gy. Heating the sample above room temperature showed increases in signal intensity. The same behaviour also occurs as the irradiated dose of the sample is increased from 1- 9 Gy. From Figure 2 (b), the intensity of signal I_2 for a given dose starts to increase rapidly after it reaches a temperature at 353 K. Korkmaz et al. [12] have reported different finding that further heating the irradiated potassium tartrate shows decreases in the signal intensity. Stronger EPR signal at high temperature in this study,

occur due to the shortening of relaxation times with temperature [13]. This is opposite from what one expects from the Bolzmann population changes.

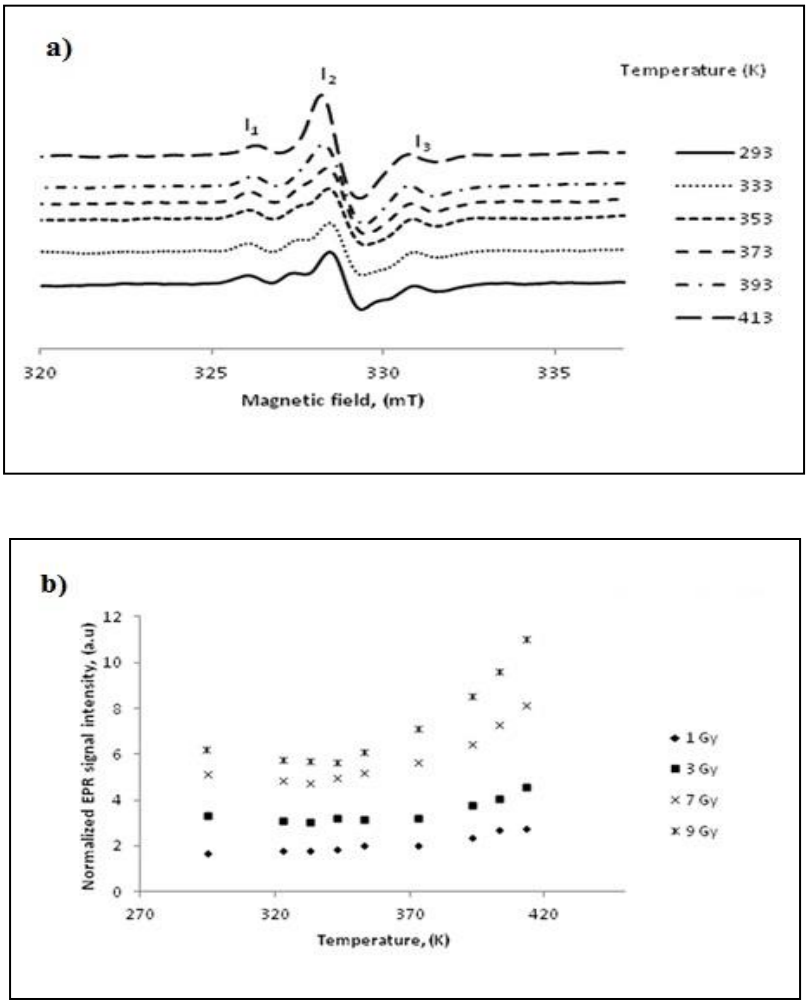

Figure 2. (a) The variation of EPR spectra recorded at different temperature for PT irradiated at a dose of 9 Gy. (b) The EPR signal intensity of PT sample (I_2) irradiated at 1, 3, 7 and 9 Gy recorded at different temperature.

The behaviour of two other signals which is signal I_1 and I_3 was also investigated to determine whether these two signals are affected by high temperature. Data obtained from a sample irradiated at 9 Gy recorded at different temperature were given in Figure 3.

Data of signal I_1 and I_3 from samples irradiated at 1, 3 and 7 Gy also give the same pattern with sample irradiate at a dose of 9 Gy. So that, only data for sample irradiated at 9 Gy is shown here. The signal intensity was normalized to their values at room temperature. The behaviour of signal I_1 and I_3 due to the high temperature is different from signal I_2. Heating the sample above room temperature showed that, the signal intensity of both signals first increased and then decreased continuously. Signal I_1 and I_3 reach its maximum value at 373 K and 393 K respectively. The decreased in signal intensity occurs due to the transition of unpaired electron from upper state to the low state of energy level.

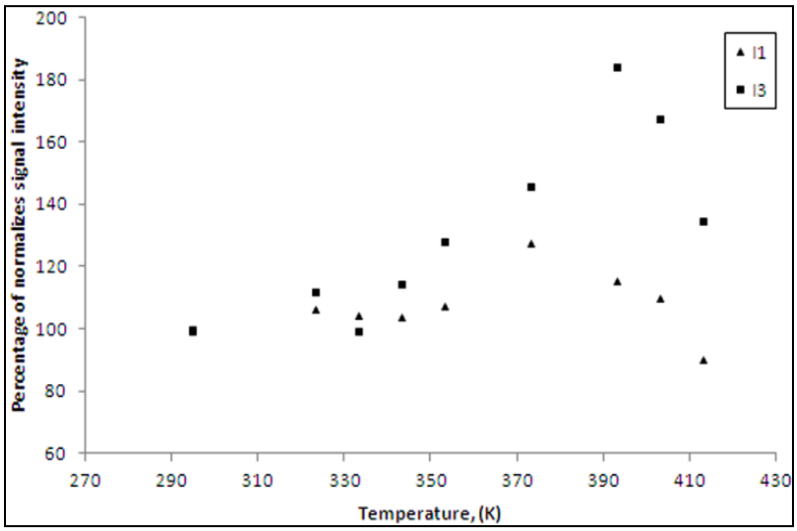

Figure 3. Variation of the EPR signal intensity of I_1 (filled triangle) and I_3 (filled square) for a sample irradiate at a dose of 9 Gy at different temperatures.

For the dose response study, PT samples irradiated to doses of 1, 3, 5, 7 and 9 Gy were used to construct the dose response curves recorded at different temperatures. Measured signal intensities from recorded spectra, I_2 was used because its dominant the entire spectra. It was then normalized to the mass of the samples. The results are presented in Figure 4. It concludes that a linear function of the type Y= ax + b was best fitted to describe the experimental data. In this function, Y and X represent as peak-to-peak signal intensity and applied dose in Gy respectively. The calculated parameter values describing the dose response function were given in Table 1 and also represented as dashed lines in Figure 4. The slope of the dose response curve (sensitivity) was found to be increased as the temperature increased.

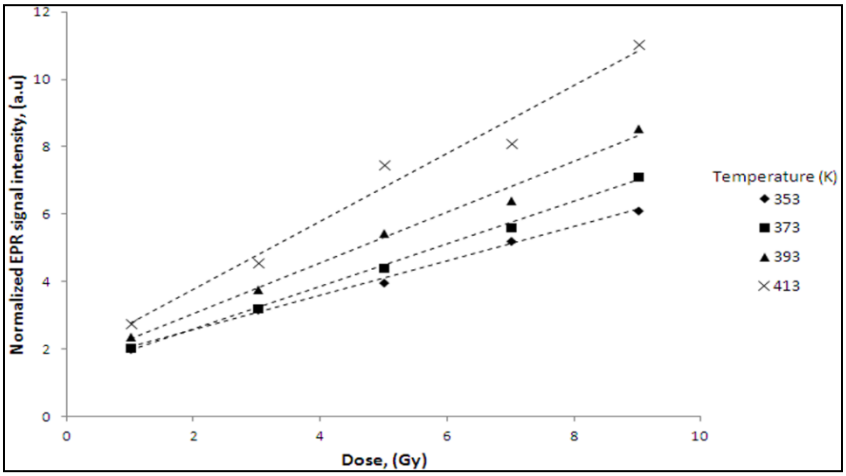

Figure 4. Variation of dose response curve of PT at different temperatures.

Table 1. Calculated parameters for a linear function describing the dose response data at different temperatures.

Temperature (K)	Parameters		Correlation coefficient
	Sensitivity, a (±)	Y-intercept, b (±)	r^2
353	0.51 (0.02)	1.54 (0.09)	0.9986
373	0.63 (0.02)	1.4 (0.1)	0.9988
393	0.75 (0.05)	1.6 (0.3)	0.9946
413	1.01 (0.09)	1.8 (0.5)	0.9875

Conclusion

From the observation, given the heat above room temperature to unirradiated PT exhibits no EPR signal, but gamma irradiated PT shows the EPR spectrum with 3 resonance lines recorded at different temperatures. These results indicate that gamma radiation can generate radicals in PT samples, but thermal energy source alone does not have enough energy to produce radicals responsible for resonance signals. This property makes PT suitable for use as an EPR dosimetry material because the radical yield for this material is not influenced by thermal energy. For irradiated PT, all 3 resonance signal intensity is affected by high temperature. The behaviour of two other resonance signals regarding to its signal intensity at high temperature gives a different pattern as compared to the main strong signal. Furthermore, the linearity of the dose response curve in gamma irradiated PT at different recording temperature indicates that this material can be used to measure radiation dose in the range of 1 Gy to 9 Gy.

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References

1. Ranby, B. and Rabek, J. F. (1977). ESR Spectroscopy in Polymer Research. Springer-Verlag Berlin Heidelberg, Germany: 1 – 53.
2. Brustolon, M. and Giamello, E. (2009). Electron Paramagnetic Resonance: A Practitioner's Toolkit. John Wiley & Sons, Inc., Hoboken, New Jersey:325 – 374.
3. ICRU Report 80. (2008). Dosimetry systems, International Commission on Radiation Units and Measurement.
4. Vestad, T. A. Malinen, E., Lund, A., Hole, E. O. and Sagstuen, E. (2003). EPR dosimetric properties of formates. *Applied Radiation and Isotopes*. 59: 181 – 188.
5. Lund, E., Gustafsson, H., Danilczuk, M., Sastry, M. D., Lund, A., Vestad, T. A., Malinen, E., Hole, E. O. and Sagstuen, E. (2005). Formates and dithionates: sensitive EPR-dosimeter materials for radiation therapy. *Applied Radiation and Isotopes*. 62: 317 – 324.
6. Gustafsson, H., Lund, A. and Lund, E. (2011). Potassium dithionate EPR dosimetry for determination of absorbed dose and LET distributions in different radiation qualities. *Radiation Measurements*. 46: 936 – 940.
7. Baran, M. P., Bugay, O. A.. Kolesnik, S. P., Maksimenko, V. M., Teslenko, V. V., Petrenko, T. L. and Desrosiers, M. F. (2006). Barium dithionate as an EPR dosemeter. *Radiation Protection Dosimetry*. 120 (1 – 4): 202 – 204.
8. Olsson, S. K., Bagherian, S., Lund, E.; Carlsson, G. A. and Lund, A. (1999). Ammonium tartrate as an ESR dosimeter material. *Applied Radiation and Isotopes*. 50: 955 – 965.
9. Polat, M. and Korkmaz, M. (2009). The effects of temperature on ESR spectrum of gamma-irradiated ammonium tartrate. *Radiation Physics and Chemistry*. 78: 966 – 970.
10. Brai, M., Gennaro, G., Marrale, M., Tranchina, L., Bartolotta, A. and D'Oca, M. C. (2007). ESR Response to ^{60}Co-rays of ammonium tartrate pellets using Gd_2O_3 as additive. *Radiation Measurement*. 42: 225 – 231.
11. Ikeya, M., Hassan, G. M., Sasaoka, H., Kinoshita, Y., Takaki, S. and Yamanaka, C. (2000). Strategy for finding new materials for ESR dosimeters. *Applied Radiation and Isotopes*. 52: 1209 – 1215.

12. Korkmaz, G., Özsayın, F. and Polat, M. (2011). An electron spin resonance (ESR) investigation of the dosimetric potential of potassium tartrate. *Radiation Protection Dosimetry*. 48: 337 – 343.
13. Ewing, G. W. (1997). Analytical Instrumentation Hanbook, 2nd ed., Revised and Expanded, Marcel Dekker, Inc., New York, USA.