Radiation Protection Dosimetry (2006), 1 of 3
doi:10.1093/rpd/nci531

BARIUM DITHIONATE AS AN EPR DOSEMETER

M. P. Baran[1], O. A. Bugay[1], S. P. Kolesnik[1], V. M. Maksimenko[1], V. V. Teslenko[1], T. L. Petrenko[1] and M. F. Desrosiers[2,*]
[1]Institute of Semiconductor Physics, Kiev, Ukraine
[2]National Institute of Standards and Technology, Gaithersburg, MD, USA

Electron paramagnetic resonance (EPR) dosimetry is growing in popularity and this success has encouraged the search for other dosimetric materials. Previous studies of gamma-irradiated barium dithionate ($BaS_2O_6 \times 2H_2O$) have shown promise for its use as a radiation dosemeter. This work studies in greater detail several essential attributes of the system. Special attention has been directed to the study of EPR response dependences on microwave power, irradiation temperature, minimum detectable dose and post-irradiation stability.

INTRODUCTION

The recent transition of the amino acid alanine dosimetry system from a reference-class dosemeter to a routine dosemeter has stimulated several new areas of research. Electron paramagnetic resonance (EPR) studies of irradiated solid alkaline-earth metals (Me) dithionates, $MeS_2O_6 \times H_2O$ have shown that they possess good properties as sensors for dosimetry[1–3]. Studies of gamma-irradiated barium dithionate ($BaS_2O_6 \times 2H_2O$) revealed a narrow and approximately isotropic EPR signal with g-factor of 2.0036 and a linewidth (ΔH_{pp}) of 0.55 mT. The radical ion SO_3^- has been proposed as a model for the radiation-induced paramagnetic centre. Weak additional satellite EPR signals with splitting of 11.5 mT were observed and attributed to the hyperfine isotropic splitting due to ^{33}S isotopes[1]. The main advantage of dithionates in dosimetry is the comparatively narrow EPR signal. As a dosemeter, $BaS_2O_6 \times 2H_2O$ was found to be usable up to 5×10^4 Gy with an uncertainty of 6%[4]. The system's long-term stability is exceptional in that the EPR signal amplitude was stable (within 5%) for $\geq$2 y[4]. This work aims to explore the effects of several EPR dosimetry parameters. Special attention has been directed to the study of measurement dependences on microwave power, irradiation temperature, minimum detectable dose and post-irradiation stability.

MATERIALS AND METHODS

Varian E12 (ISP, Kiev) and EleXSys (NIST, Gaithersburg) EPR spectrometers were used. The barium dithionate dihydrate was synthesised according to a previous synthesis[5]. Both tablet and powder samples were used for EPR experiments. The tablets were 4.8 mm in diameter and 5 mm in height, with an average mass of 170 mg. Powder samples for EPR measurements were inserted in 10 mm sections of a cut 5 mm diameter EPR sample tube, and the ends of the tube were closed with plastic plugs. For gamma irradiation, powder samples were placed in polyethylene packets. Gamma irradiation was delivered using the ^{60}Co and ^{137}Cs vertical beam (B036) sources of the NIST Ionizing Radiation Division, and the MPX-25 ^{60}Co Gamma-cell and ^{137}Cs source in Kiev.

RESULTS AND DISCUSSION

The shape of the EPR spectrum depends on the microwave power (Figure 1). Two different EPR signals are clearly observed. The narrow signal, R_1, is observed at low powers (0.02–0.2 mW) and has gaussian form. This signal saturates with increasing power. The broad signal R_2 appears at 2 mW and increases with increasing power. At maximum power, 200 mW, both signals are observed. The signal shape of R_2 is also gaussian. At a microwave power of 200 mW the signal R_2 is partly saturated.

The maximum-likelihood common factor analysis (MLCFA) of these spectra confirms the conclusion that the observed spectrum is the superposition (sum) of the only two spectra, R_1 and R_2, and that the concentrations of these two centres differ by no more then 15%[6]. Parameters of the EPR spectra have been determined. The g-factors for R_1 and R_2 are 2.0024 and 2.0025, respectively. Super hyperfine structure parameters are (in 10^{-4} cm^{-1}) $A_1 = 143.8$, $A_{2,3} = 115.5$ for R_1 and $A_1 = 133.3$, $A_{2,3} = 100.0$ for R_2 centres. The linewidths (ΔH_{pp}) for R_1 and R_2 are 0.32 and 1.2 mT, respectively.

The dependence of the EPR signal amplitude on absorbed dose was studied up to 100 Gy using the ^{137}Cs source of the Interdisciplinary Scientific and Technical Centre in Kiev, and for absorbed doses up to 16.95 kGy using ^{60}Co Gamma Cell of the Institute of Physics in Kiev. The dose dependence is linear up

*Corresponding author: marcd@nist.gov

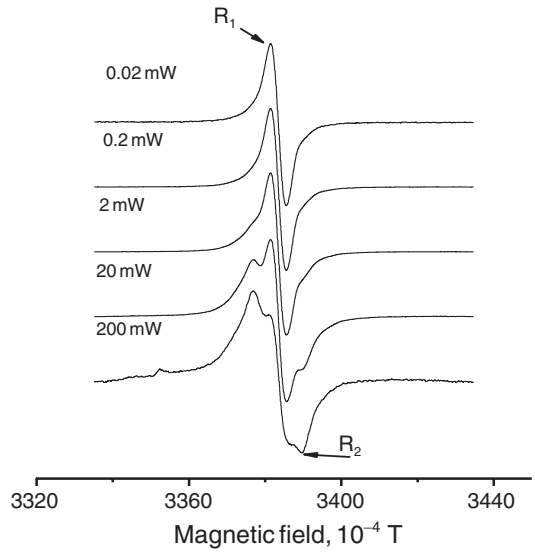

Figure 1. The EPR spectra measured at different microwave powers (see labels). Symbols R_1 and R_2 correspond to different radiation-induced centres. A gamma-irradiated (1 kGy) powder sample of barium dithionate was measured by using a Varian E12 spectrometer.

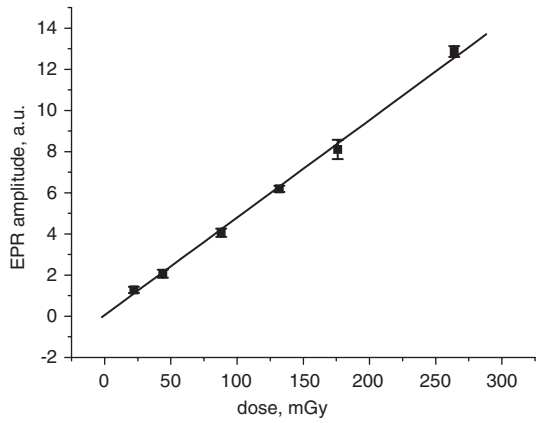

Figure 2. A graph of the barium dithionate radiation-induced EPR amplitude and absorbed dose.

to 2 kGy and the EPR response saturates thereafter. For unirradiated samples, the resulting spectrum is equivalent to a zero response ($\sigma = 0.003$ Gy).

To determine the dose detection limit (or low-dose threshold) for the barium dithionate samples the intensities of the EPR radiation responses to irradiation dose were measured using the Varian EPR E12 spectrometer. Six groups of five samples each were irradiated at doses from 22 to 264 mGy using a ^{137}Cs source. These data (Figure 2) were used to calculate the low-dose threshold using the ISO 11843 method[7]. The experimental data are assumed to be homoscedastic and all 30 experimental points were included in the calculation. The low-dose threshold is 9 mGy ($\alpha = 0.05$).

The EPR signal amplitude can change after irradiation and this effect depends on the storage temperature. To study this effect, a relatively large barium dithionate powder sample (2 g) was irradiated with a dose of 50 Gy. Then the sample was divided into 35 (0.2 g) aliquots. Four sets composed of seven samples each were stored for ~2 months at the following temperatures: 30, 40, 50 and 60°C. Periodically samples were selected and the EPR spectral amplitudes were measured. The EPR signal amplitude decreased significantly (>50%) during the first month of storage at 60°C. At the other temperatures, the EPR signal amplitudes remained within a percentage of the original measurement for the entire measurement period (~2 months).

For dosimetry comparison purposes, barium dithionate and alanine tablets were prepared with the same geometrical size, 4.9 mm diameter and 5 mm height. The tablet masses were 88 mg for alanine and 190 mg for barium dithionate. The tablets were co-located and co-irradiated in a ^{60}Co Gammacell to a dose of 800 Gy. The spectrum for each sample was measured at the optimal spectrometer settings for each substance. The EPR spectrometer parameters (for the E12 Varian spectrometer and E-232 dual sample microwave cavity) were the same except for the magnetic field modulation amplitude (0.4 and 0.8 mT for barium dithionate and alanine, respectively, owing to their different EPR signal widths) and microwave power (1.0 and 10.0 mW, respectively, owing to the difference in their saturation characteristics). Under these conditions the ratio of the peak-to-peak EPR line of barium dithionate to the central line of the alanine is 10.4.

The radiation yield (G-value) for alanine was determined to be 2.5×10^{14} spin (g Gy)$^{-1}$ by comparison to Varian strong pitch using the method described below; this value is identical to the literature value[8]. The G-value for the barium dithionate was evaluated by comparing the EPR responses in alanine and barium dithionate irradiated to the same absorbed dose (1100 Gy). The double integral of the EPR spectrum for both samples were compared using the same EPR spectrometer parameters, including the same level of microwave power and the same magnetic field modulation amplitude. The resulting value for the radiation yield of barium dithionate is 8×10^{13} spin (g Gy)$^{-1}$ ($\sigma = 2 \times 10^{13}$). This value is comparable with a previously determined G-value for barium dithionate[4].

For most chemical dosemeters their response to the absorption of ionising radiation is dependent on temperature. Correcting the response of a dosemeter to that of the temperature at which the dosemeters

were calibrated improves the accuracy of the dosimetry. To measure the temperature dependence, two identical cylindrical plastic foam thermostats were prepared[9]. Both thermostats were filled with the same volume of water, at a temperature of 0°C in one and 40°C in the other. Powder samples of barium dithionate were placed in identical hermetically sealed glass tubes of 5 mm diameter, centred along the axes of the thermostat. The thermostats were stacked in the centre of the cylindrical ^{60}Co Gammacell sample chamber. The irradiation was divided into two equal parts: during the first irradiation (120 s) the 40°C thermostat was placed in the top position, and in the second irradiation (also 120 s), the 40°C thermostat was in the bottom position. This was done to remove any influence of the heterogeneity of the radiation field in the chamber. The thermostat temperature was measured with a thermocouple, and during irradiation the temperature changed ~0.5°C. The temperature coefficient was estimated to be 0.10% K^{-1} ($\sigma = 3\%$). The temperature coefficient for alanine is ~0.15% K^{-1}[10].

CONCLUSION

The dosimetric attributes of barium dithionate show possibilities for several radiation applications. The low-temperature coefficient and superior stability characteristics are particularly notable. Industrial, medical and accident dosimetry could all benefit from the higher sensitivity of this system.

DISCLAIMER

The mention of commercial products throughout this paper does not imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that products identified are necessarily the best available for this purpose.

REFERENCES

1. Bogushevich, S. E., Makatun, V. N., Potapovich, A. K. and Ugolev, I. I. *Peculiarities of the thermoradiation destruction* $BaS_2O_6 \times 2H_2O$. Zh. Prikl. Spectrosc. **55**, 613–618 (1991).
2. Bogushevich, S. E., Ugolev, I. I. and Potapovich, A. K. *Production of* SO_3^- *ion-radicals in barium dithionate exposed to ionizing radiation.* J. Appl. Spectrosc. **63**(2), 207–212 (1996).
3. Lund, A., Olsson, S., Borona, M., Lund, E. and Gustafsson, H. *New materials for ESR dosimetry*. Spectrochim. Acta A **58**, 1301–1311 (2002).
4. Bogushevich, S. and Ugolev, I. *Inorganic EPR dosimeter for medical radiology*. Appl. Radiat. Isot. **52**(5), 1217–1219 (2000).
5. Brauer, G. *Handbuch der Preparativen Anorganischen Chemie* (Auflage: Ferdinand Enke Verlag Stuttgart. I) p. 358 (1975).
6. Moens, P., De Volder, P., Hoogewijs, R., Callens, F. and Verbeeck, R. *Maximum-likelihood common-factor analysis as a powerful tool in decomposing multicomposite EPR powder spectra*. J. Magn. Reson. A **101**, 1–15 (1993).
7. International Organization for Standardization. *Capability of detection—Part 2: methodology in the linear calibration case*. ISO 11843-2:2000(E) (Geneva: ISO) (2000).
8. Box, H. C. and Freund, H. G. *Paramagnetic resonance show radiation effects*. Nucleonics **17**(1), 66–76 (1959).
9. Bugay, A., Kolesnik, S., Mehta, K., Nagy, V., Desrosiers, M. F. *Temperature stabilization of alanine dosimeters used for food processing and sterilization*. Appl. Radiat. Isot. **52**, 1371–1373 (2000).
10. Nagy, V., Puhl, J. M. and Desrosiers, M. F. *Advancements in accuracy of the alanine dosimetry system. Part 2. The influence of the irradiation temperature*. Radiat. Phys. Chem. **57**(1), 1–9 (2000).