THE POSSIBLE USE OF $K_2CH_2(SO_3)_2$ AND $NAHCO_2$ AS ALTERNATIVE MATERIALS IN EPR RADIATION DOSIMETRY

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Abstract

This paper reported the work on electron paramagnetic resonance (EPR) spectrometry of some inorganic materials in radiation dosimetry area. These materials are $K_2CH_2(SO_3)_2$ and $NaHCO_2$. The aim was two: *first*, to access the EPR spectra measured from the radicals *sulphur trioxide anion* (SO_3^-) in γ-irradiated $K_2CH_2(SO_3)_2$ and *carbon dioxide anion* (CO_2^-) in γ-irradiated $NaHCO_2$ and to justify whether their performance might approach the similar performance of alanine, a radiation dosimetry standard material. Thus far, the intensity of EPR spectrum of γ-irradiated alanine has been accepted by the International Atomic Energy Agency (IAEA) as a secondary standard for high-dose (10-10^5Gray) dosimetry. *Second*, to discover a dosimetry material that sensitive enough to function in the "clinical" dose range, that is below 10 Gray. A radiation plant of ^{60}Co Gammacell 220 operates at room temperature was occupied to irradiate the samples. EPR measurement was carried out by a Varian E-12 EPR spectrometer. By using a readout parameter of the peak-to-peak excursion of the strongest line of the systems, some important findings were noted and reported in this paper.

Keywords: *$K_2CH_2(SO_3)_2$, $NaHCO_2$, SO_3^- and CO_2^- radicals, EPR, radiation dosimetry.*

INTRODUCTION

Radiation dosimetry recently has become an active application of electron paramagnetic resonance (EPR) spectroscopy in monitoring irradiation of food as well as in searching a dosimetry material that sensitive enough to use as a radiotherapy monitor. Since 1960s (Bradshaw *et al*., 1962), irradiated L-α-alanine (abbreviated as "alanine") has been employed as a standard dosimetry material in the high dose range between 10-10^5 Gray. The peak-to-peak distance of the first derivative of the central line of the spectrum of the stable alanine radical (SAR) $CH_3\dot{C}HCOO^-$ (see Figure 1a) has been suggested as the dosimeter readout in order to measure the dose absorbed. Performance of the EPR/alanine dosimeter also has been validated by many workers. Further, due to some important requirements met by the EPR/alanine dosimeter, the International Atomic Energy Agency-IAEA (Nam, J.W. *IAEA Bulletin*, 1988) has recommended alanine as the dosimeter choice on the above dose range. Those requirements are included: (a) linearly increase of the signal with the dose over a wide range, (b) no signal fading was observed during certain period of time storage, and (c) "water equivalent" of the material, *that is*, a material that as nearly as possible duplicated the response of water, and hence human tissue, to the effects of radiation of various kinds.

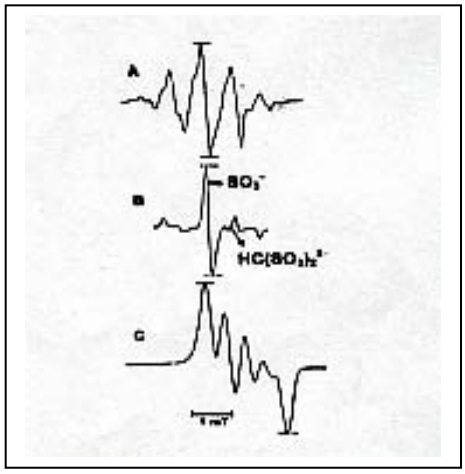

Figure 1: The first-derivative EPR spectra due to: **(A)** $CH_3\dot{C}HCOO^-$ radical in γ-irradiated alanine. **(B)** SO_3^- radical (in the wings) in γ-irradiated $K_2CH_2(SO_3)_2$. **(C)** CO_2^- in irradiated $NaHCO_2$. Experimental conditions were set as given in the text.

EPR/alanine dosimetery, however, is not without disadvantages for some reasons, namely (a) the signal actually span along 10 mT. Thus employing of the intensity of the central line means a loss of potential sensitivity. (b) The spectrum is so complex (Ermawati, F.U. *Indonesian Journal of Physics*, 2001) that it does not lend itself to accurate double integration. (c) At microwave power level more that 10mW, *spin-flip* satellites steal intensity from the central peak and this invalidates the readout (Arber, J.M., *et al*., *Appl. Radiat. Isot.* 1991), means that increased microwave power level cannot be used in an attempt to gain sensitivity. (d) At a received dose of 10 Gray, the signal is comparable to the noise level of a modern spectrometer operated at high gain but without computer enhancement.

Further, when properly calibrated, alanine dosimeter is capable of something like ± 2% precision in the high-dose range. It is unsuitable as a *clinical* or low-dose range dosimeter (< 10 Gray), at least until spectrometer sensitivities improve. Thus, it seems that there is an essential need for new dosimeters in the clinical or low dose range above. For example, typical radiotherapy of cancer patients is a course of 6-10 treatments of calculated as 1 Gray. Greater precision and the possibility of instant readout would be highly beneficial in such treatments.

Furthermore, even as a high-dose ranges dosimeter, alanine may not be the best, only the best so far investigated. Ideally, one requires a substance that on irradiation produces an EPR spectrum consisting of a single and sharp line, which means no hyperfine structure and an isotope g-factor. The signal must increase linearly with the dose over a wide range, and preferable be detectable in a 50 mg sample with a dose of 1 Gray or less. It is therefore the purpose of this present paper to report the investigation result on such a dosimeter.

EXPERIMENT

About 50 mg samples of possible dosimeter materials of $K_2CH_2(SO_3)_2$ and $NaHCO_2$, each were irradiated at room temperature in ^{60}Co Gammacell 220 The dose rate was 0.24 kGray per hour (Instruction Manual and Owner's Guide Gammacell 220, 1980). 50 mg of L-α-alanine silicon pellets (Ermawati, 2003), that used as standard samples, were also irradiated to doses between 1 and 10 Gray in order to provide a basis of comparison between standard alanine and the new materials mentioned above. EPR measurements were carried out with a Varian E-12 EPR spectrometer just after completion of the irradiation process. X-band, continuous wave of first-derivative absorption lines was recorded from the spectrometer under the standard conditions: microwave power of 2 mW, field modulation at 100 kHz was 0.5 mT, magnetic field was set to 336 mT, the scan is 20 mT and linear sweep in 8 minutes. The receiver gain was varied to record visible and readable signals on the chart. All measurements were performed at room temperature and the relative humidity was 50 ± 2%. Finally, the signals obtained from the new materials were compared

with those obtained from alanine on graphs of log (signal height/gain) against log (dose/Gray), see Figures 2 and 3.

RESULTS AND ANALYSIS

Sulphur Trioxide Anion (SO_3^-) radical.

The first system examined as an alternative dosimeter to alanine was *potassium methionate,* $K_2CH_2(SO_3)_2$. The first radical observed in the system was *sulphur trioxide anion* (SO_3^-). This species may be trapped in a variety of matrices and found to be stable against decay. The radical has an isotropic g-factor of 2.0036. There was no hyperfine structure except that of the isotopes ^{33}S and ^{17}O, neither of which was present abundance of greater than 1%. Thus, the spectrum of SO_3^- in powders is that of a single line (see Figure 1B), one of the ideal characteristics mentioned above. Radical SO_3^- was examined in irradiated potassium methionate, because in that matrix the ^{33}S hyperfine structure had been detected in natural abundance, indicating a very strong signal from SO_3^- containing the normal isotopes.

The only disadvantage of the $K_2CH_2(SO_3)_2$ matrix is the presence of weaker signals from the radical $HC(SO_3)_2^{2-}$. However, as seen in Figure 1B, the spectrum of the second mentioned radical did not interfere with that of SO_3^- because the proton hyperfine interaction matrix in $HC(SO_3)_2^{2-}$ did not have a principal value approaching zero, and hence did not contribute to the intensity of the central line. Further, the intensity of the SO_3^- signal in 50 mg γ-irradiated $K_2CH_2(SO_3)_2$, that was measured as the peak-to-peak distance of the first-derivative lines, is compared with that in 50 mg pellets of alanine (see Figure 2). As a function of dose absorbed and under the same experimental conditions, it was obtained that signal intensities of the two samples are linearly increase and parallel to each other, indicating that the dose response of $K_2CH_2(SO_3)_2$ sample is comparable with that of the standard alanine. Furthermore, using the central line of the alanine spectrum as the readout parameter, signal from SO_3^- was about 3.5 times stronger than that of alanine at the same dose level. Moreover, the SO_3^- signal in Figure 1B is a single line, and should lend itself to computerized integration with greater accuracy than the complex alanine spectrum. The features in the wings (due to $HC(SO_3)_2^{2-}$ radical) are sufficiently distinct from the central feature (SO_3^-) that they could readily be eliminated from the integration.

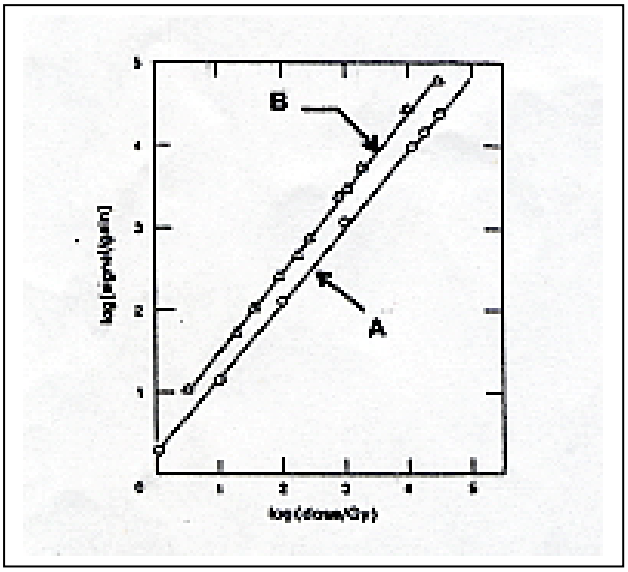

Figure 2: EPR signal intensity as a function of dose of a 50 mg: **(A)** alanine-silicone pellets dosimetry, and **(B)** SO_3^- in $K_2CH_2(SO_3)_2$. Both signals were recorded at 2 mW power level. The Experimental condition is given in the text.

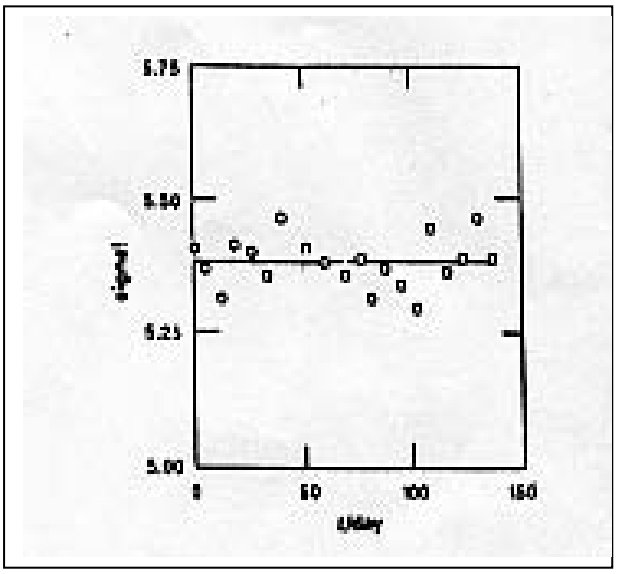

Figure 3: Signal intensity of SO_3^- radical as a function of time (days) in potassium methionate. The sample was γγ-irradiated to a dose of 10^4 Gray. The straight line is a least-square fit to the experimental data points. Experimental condition is as mentioned in the text.

In addition, in terms of stability of signal, the SO_3^- signal in $K_2CH_2(SO_3)_2$ met the principal requirement for a dosimeter, *that is*, it is completely stable over a period of time. Thus, the intensity of the signal at room temperature (± 25°C) was monitored for a period of 150 days (see Figure 3). Every effort was made to position the sample in exactly the same place in the cavity everyday, and of course, the experimental conditions were set always the same. The spectrometer was also allowed to warm up in operating mode for about 1 hour before taking the measurement. Referring back to Figure3, the scatter in the position of the data point in that figure represents a random fluctuation in spectrometer sensitivity that was calculated as about 2.5%, *that is*, a fluctuation of unknown origin. However, upon fitting the data points to a straight line by the method of least squares, within experimental error, the line was found to have a zero slope. In other words, over a period of 150 days the decay of SO_3^- in $K_2CH_2(SO_3)_2$ was infinitely small.

Another important result performed by the $K_2CH_2(SO_3)_2$ system is that the SO_3^- radical signal is optimum at 7 mW, above which power level it decreases rapidly. It is therefore the SO_3^- radical suffers from the same defect as that of $CH_3\dot{C}HCOO^-$ in alanine, and could not be used at high microwave powers for greater sensitivity. Unfortunately, the presence of potassium and sulphur in the host compound has become a disadvantage of SO_3^- in $K_2CH_2(SO_3)_2$ system, as these elements will undoubtedly affect the water equivalence of $K_2CH_2(SO_3)_2$, and thus its potential use as a dosimeter.

Carbon Dioxide Anion (CO_2^-) radical

Trapping of the carbon dioxide anion (CO_2^-) radical in irradiated sodium formate ($NaHCO_2$) had been studied a long ago by Ovenall and Whiffen (Ovenall, *et al.*, 1961). In that study, the radical CO_2^- (see Figure 1C) was trapped near a sodium ion (I = 1.5) whose hyperfine interaction dominated the spectrum. If this CO_2^- spectrum was compared to that of SAR in alanine (Figure 1A) and that of SO_3^- in potassium methionate (Figure 1B), it was obtained that the spectrum due to CO_2^- in $NaHCO_2$ has one advantage over both the spectra due to SAR radical in alanine and that of SO_3^- in potassium methionate, *that is* the spectrum does not become saturated below 80 mW. Hence, in contrast to the other dosimeters, $NaHCO_2$ has the capacity for increased sensitivity with increased microwave power. Figure 4 below shows the comparison between the signal intensities (as a function of dose) recorded from CO_2^- in sodium formate at 80 mW (B) and that of SAR radical in alanine at 2 mW (A). It was obtained that sodium formate is more sensitive by a factor of 3.5.

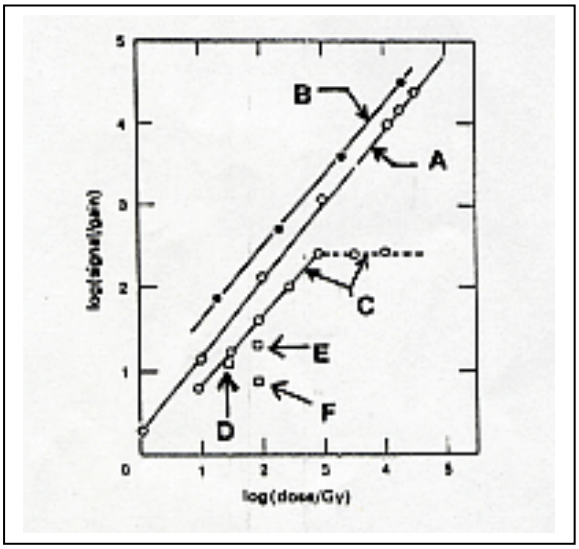

Figure 4: EPR signal intensities as a function of dose of a 50 mg of: (**A**) alanine-silicone pellets dosimetry (2 mW); (**B**) CO_2^- in sodium formate (80 mW); (**C**) CO_2^- in $CaCO_3$ (2 mW); (**D**) adamantan; (**E**) $(C_6H_5)_3CH$, and (**F**) $(C_6H_5)_3COH$. Experimental conditions are given in the text.

However, at the same dose level of 10^4 Gray, the CO_2^- signal in $NaHCO_2$ (see Figure 5) was not stable against decay as was SO_3^- signal in $K_2CH_2(SO_3)_2$ (see again Figure 3). It was observed in Figure 5 that the CO_2^- signal decayed by 30% over the first six weeks. Thus, further experiments are recommended to determine whether the signal in the sample irradiated to 10^3 Gray or less decays in a similar manner or not.

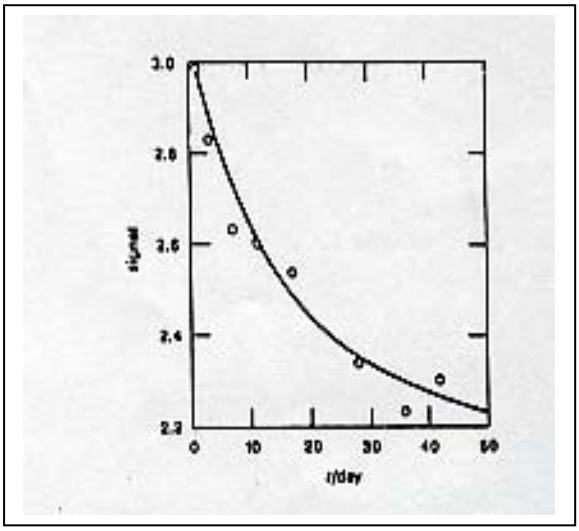

Figure 5: Signal decay of the CO_2^- radical in sodium formate irradiated to a dose of 10^4 Gray. Experimental condition was set as in text.

Further, in any event there may be other matrices in which CO_2^- is totally stable against decay. In this work, examination to the spectrum of (CO_2^-) in irradiated $LiHCO_2$ and $CaCO_3$ was also carried out. The spectrum of (CO_2^-) in $LiHCO_2$ was found weak, and the main radical species produced was HCO_3, whose large proton hyperfine interaction causes it to be useless for dosimetry purposes. In $CaCO_3$, however, CO_2^- exhibits a reasonably strong signal, consisting of a single line at g = 2.001. In Figure 4C, this signal (at 2 mW) is compared to that of $CH_3\dot{C}HCOO^-$ in alanine (A). It was found that the signal starts to saturate at 10^3 Gray and was also slightly weaker than that of alanine at the same power level (2 mW).

Other possible organic dosimeters

A few experiments on certain organic materials that on irradiation gave single-line EPR spectra were also carried out. Those included *adamantan-l*, *triphenyl methane* and *triphenyl methanol*. Unfortunately, the results (see Figure 4D-F) were disappointing; since in those systems the signal height was much less than that of the central peak from a equal weight of alanine (50 mg).

CONCLUSION

The series of investigation to improve performance of the EPR/alanine dosimetry has been undertaken. It comes out that SO_3^- in $K_2CH_2(SO_3)_2$ is at least as good as $CH_3\dot{C}HCOO^-$ in alanine, and in certain conditions it is better, although it will have an undesired water equivalence. The signal from CO_2^- in $NaHCO_2$, although suffering from the disadvantage of the presence of ^{23}Na hyperfine structure, can be operated at up to 80 mW, with a consequent potential for increased sensitivity. The two alternative dosimetry materials above are capable of operation at 10 Gray, without computer enhancement of the signal. As a result, they approach the sensitivity required by a clinical dosimeter that must operate in the range below 10 Gray. Further, since SO_3^- and CO_2^- radicals can be trapped in a wide variety of matrices, it may be possible to discover a dosimeter material in which one of them can be trapped in higher concentrations than that of described here.

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