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Can Ammonium Tartrate Replace Alanine in EPR Radiation Dosimetry? †

Ahmed Mohamed Maghraby [1,*], Ahmed Soltan Monem [2] and Hoda Mohamed Eissa [1]

[1] Radiation Dosimetry Department, National Institute for Standards (NIS), Ministry of Scientific Research, Haram, P.O. Box 136, Giza 12211, Egypt; ho_eissa@yahoo.com
[2] Biophysics Department, Faculty of Science, Cairo University, Giza 12613, Egypt; maghrabism@gmail.com
* Correspondence: maghrabism@yahoo.com; Tel.: +20-12-70129147
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Abstract: EPR, which is characterized by the non-destructive evaluation of radiation-induced radicals, is one of the most recent and accurate techniques for radiation dose measurements. Alanine has been considered the reference EPR dosimeter for several applications over decades due to its consistent response and the stability of its radiation-induced radicals. Recently, ammonium tartrate was proposed as a promising EPR dosimeter, as it possesses several prominent dosimetric features. In this work, ammonium tartrate is investigated as a possible alternative to alanine. The studied properties include sensitivity to different radiation doses, energy dependence, detection limit, and the stability of the induced radicals. Ammonium tartrate's responses to Cs-137 gamma radiation were studied and compared with those of alanine over two ranges: the first ranged from 47 to 2500 Gy, and the second ranged from 1.46 to 87.8 Gy. The uncertainties associated with the evaluated radiation doses using EPR/the ammonium tartrate dosimetry system were evaluated and are presented in detail.

Keywords: radiation dosimetry; alanine; ESR; EPR; ammonium tartrate

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1. Introduction

Electron paramagnetic resonance spectroscopy (EPR) evaluates the unpaired electrons in materials and can be employed for the measurement of radiation doses. Alanine was first proposed as a radiation dosimeter in 1962 [1], and since that date, it has been considered the reference EPR dosimeter for several applications of ionizing radiation. This may be due to the exceptional dosimetric features of alanine: high stability; a wide range of proportionality to radiation doses, especially for high doses; and an energy response that matches human soft tissue properties, in addition to non-toxicity, as it is an amino acid [2].

However, there are some drawbacks that have disabled the extension of alanine dosimetry to modern medical applications; these features include its complicated EPR spectrum, which is attributed to at least three different radicals [3], and its complex time dependence, which varies with the levels of applied radiation doses [4], in addition to the limit of detection, which can hardly reach values of lower than 2 Gy [5]. Several methods have been used in order to increase the sensitivity of alanine to lower doses, such as the addition of nanoparticles [6], the use of digital filters [7], and the use of very complicated, impractical experimental procedures [8].

Several materials have been proposed as possible EPR dosimeters [9–14]; one of these is ammonium tartrate, which has been proven through extensive studies to have promising spectroscopic and dosimetric features: a simple EPR spectrum, highly stable radiation-induced radicals, and a lower limit of detection. These features were able to make ammonium tartrate the subject of more investigations for over more than two decades; this ranked ammonium tartrate second after alanine from the point of view of EPR dosimetry systems, according to a number of studies [15–20]. Other relevant studies have extended

to other tartrate compounds; these compounds are derived from tartaric acid and have some common features. However, ammonium tartrate is still considered the best among them [21–24]. This study aims to evaluate to what extent ammonium tartrate can replace alanine in EPR radiation measurements.

2. Instruments, Materials, and Methods

2.1. Radiation Source and Radiation Dose Measurements

Gamma irradiation was executed using a Cesium-137 gamma ray, model GB-150, which was fabricated by Atomic Energy of Canada Limited in April 1970; it has an initial activity of 1000 Ci. (3.7×10^{13} Bq). Air kerma (K_{air}) was measured and evaluated according to International Atomic Energy Agency (IAEA) code of practice TRS-(381) [25]. The determination of K_{air} was performed using the secondary standard dosimetry system of the National Institute of Standards (NIS)—Egypt, which was calibrated at the Bureau International des Poids et Mesures (BIPM), France. The Kair values were evaluated with an associated expanded uncertainty of about 0.9% at a 95% level of confidence (coverage factor = 2). Irradiation was executed at normal room conditions in Perspex phantom irradiation capsules; the range of radiation doses given to the dosimeters was from 1.46 Gy to 2.5 kGy.

2.2. EPR System

The EPR spectrometer used in this study was an EMX-BRUKER EPR system, manufactured in Germany, which contained a rectangular resonator 4102 ST cavity operating in the TE_{102} mode. The system also contained a 9.5 GHz microwave (X-band) Gunn oscillator bridge.

2.3. Sample Preparation and Evaluation Method

Ammonium tartrate's molecular formula is ($C_4H_{12}O_6N_2$); it has a molecular weight of 184.15 g/mol and a density of 1.6 g/cm^3. The electron density, <Z/A>, for ammonium tartrate = 0.53217. Crystals of ammonium tartrate were purchased from ADWIC and prepared as described by Prolabo (99% for purity). Samples were prepared for irradiation by being packed in the irradiation capsules, which were manufactured of leucite (Polymethyl methacrylate (PMMA)) in order to guarantee the equilibrium of charged particles during the irradiation process.

For the EPR measurements of ammonium tartrate, the parameters were the following: the microwave power was 0.6315 mW, the modulation amplitude was 0.8 mT, the field center was 348.0 mT, the sweep width was 30.0 mT, the time constant was 20.48 ms, and the conversion time was 10.24 ms for 1024 data points. Hence, the sweep time was about 10.48 s.

Empty tube spectra were measured before recording of the sample spectra in order to assure the purity of the obtained EPR signals. A reference standard material (DPPH) was used to correct the peak-to-peak amplitudes of the EPR spectra acquired before and after every single spectrum of the ammonium tartrate dosimeters, hence eliminating all possible changes in the spectrometer sensitivity.

The average mass of each ammonium tartrate dosimeter was 0.20 ± 0.014 g. Normalization of the EPR signal intensities was executed according to this value. The EPR spectrum of each dosimeter was recorded at least three successive times, each of a single scan.

3. Results and Discussion

3.1. Induced Radical

Figure 1 represents the EPR spectra of the ammonium tartrate dosimeters; Figure 1A represents the unirradiated spectrum with no distinctive features, and Figure 1B represents a singlet located at g = 2.0049. This singlet is attributed to the radical $H_4N^{+-}OOC\text{-}C^{\bullet}(OH)\text{-}CH(OH)\text{-}COO^{-+}NH_4$ [16], while in [17], thoughts of another type of radical were proposed, and there were several attempts to define the second stable radical in ammonium tartrate [20]. Both radicals shared the same approximate position; hence, this was difficult to

resolve at room temperature. Figure 2 shows the EPR spectrum of the irradiated ammonium tartrate recorded at a modulation amplitude of 0.1 mT, which confirm the presence of more than one overlapped singlet.

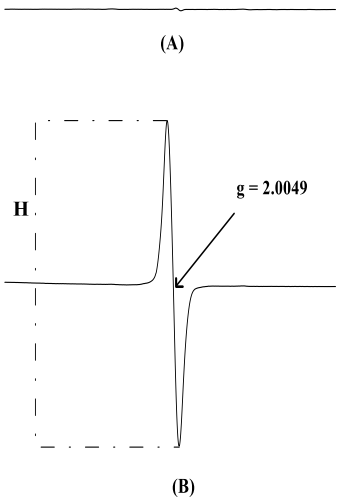

Figure 1. EPR spectra of ammonium tartrate, (**A**) the unirradiated dosimeter, and (**B**) the 850 Gy gamma-irradiated dosimeter.

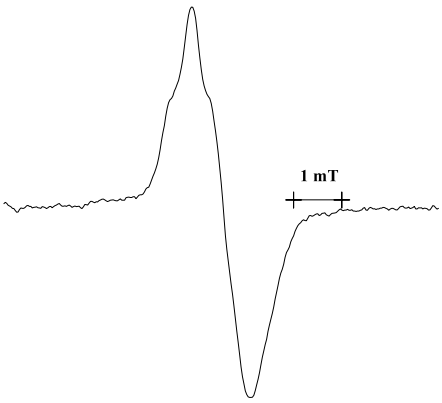

Figure 2. EPR spectrum of irradiated ammonium tartrate acquired at a 0.1 mT modulation amplitude.

3.2. Time Dependence

The time-dependence curves of H_{PP} for both the standard and ammonium tartrate dosimeters are shown in Figure 3, where it is clear that the instabilities of the peak-to-peak signal amplitude of the ammonium tartrate over the first eight hours following irradiation cannot be attributed to changes in the spectrometer sensitivity, as can be confirmed with the behavior of the standard. During the first hour, variations in H_{PP} were in the range of 0.74% and the average value showed instabilities, while during the next 3 h, the H_{PP} decreased, while the variation range was about 0.68%. After the 4th hour, the H_{PP} started to increase markedly, with a variation range of 1.39%; this behavior is partially different from in other previous studies [17,20] and suggests the presence of more than one radical species.

In Figure 4, the H_{PP} of ammonium tartrate is traced over 28 days following irradiation with four different doses. In this figure, the H_{PP} increases until day 2; however, the variations over the range of the first 3 days were (0.41–0.89)%. At the end of the study term, the H_{PP} showed a decrease to about 92% of its original value. In a previous study [20], H_{PP} started to decrease only after day 15.

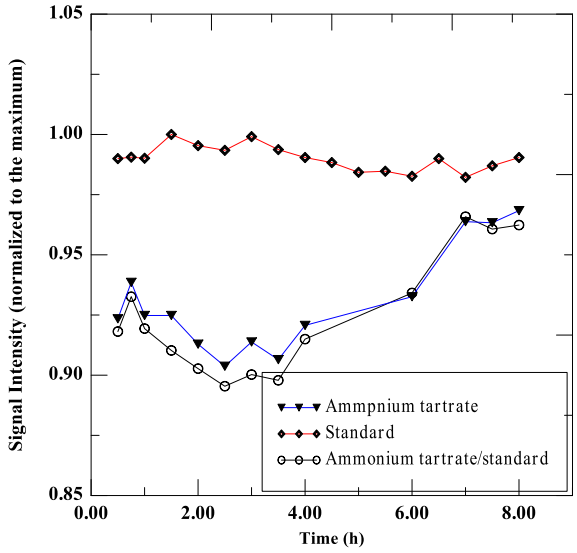

Figure 3. Short-term time dependence of H_{PP} over the first eight hours following irradiation.

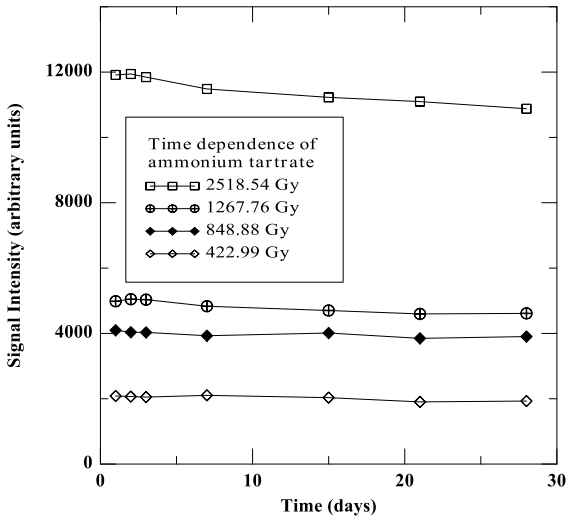

Figure 4. Long-term time stability of H_{PP} over the first 28 days following the day of irradiation.

3.3. Response to Gamma Radiation

Figure 5 represents the responses of ammonium tartrate and alanine dosimeters to the same radiation doses in the range of (44–250) Gy, and both have been fitted linearly. From the figure, it is clear that ammonium tartrate is more sensitive than alanine by a factor (on average) of about 2.1. The responses to a low radiation dose range, (1.5–78) Gy, are represented and linearly fitted in Figure 6; the ammonium tartrate dosimeters were found to be more sensitive than the alanine by a factor of 1.84 on average.

Table 1 shows the percentage precision and the associated combined uncertainties of the ammonium tartrate and alanine dosimeters for selected radiation doses over a wide range of (0.57–2500) Gy. This table confirms the superior dosimetric features of ammonium tartrate over the corresponding parameters of alanine; the ammonium tartrate shows a better percentage resolution and lower uncertainties, especially for low radiation doses.

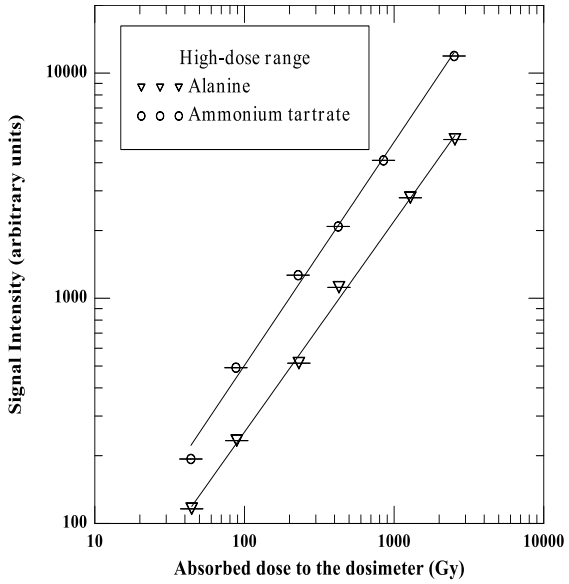

Figure 5. Responses of H_{PP} to radiation doses in the range of (44–2500) Gy for both alanine and ammonium tartrate.

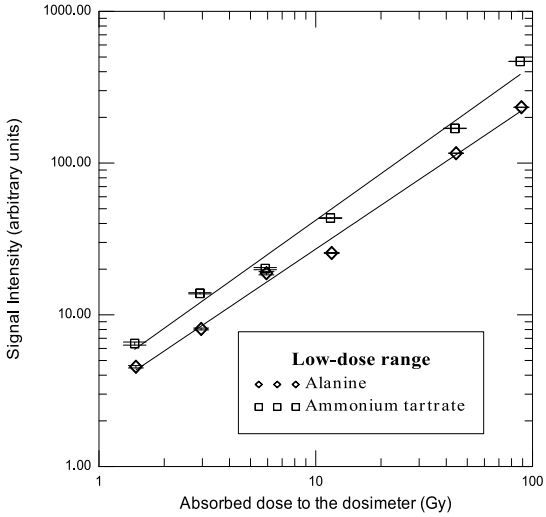

Figure 6. Responses of H_{PP} to radiation doses in the range of (1.5–88) Gy for both alanine and ammonium tartrate.

Table 1. Percentage precision and the associated combined uncertainties for ammonium tartrate and alanine dosimeters for selected values of radiation doses.

Air Kerma (Gy)	Ammonium Tartrate		Alanine	
	Percentage Precision	Combined Uncertainty	Percentage Precision	Combined Uncertainty
2500	0.06	0.48	0.14	0.48
1230	0.17	0.48	0.13	0.48
824	0.21	0.48	0.40	0.48
410	0.14	0.48	0.65	0.49
221	0.67	0.49	0.28	0.48
85	1.61	0.50	0.78	0.49
42	2.52	0.55	1.30	0.50

Table 1. *Cont.*

Air Kerma (Gy)	Ammonium Tartrate		Alanine	
	Percentage Precision	Combined Uncertainty	Percentage Precision	Combined Uncertainty
11	3.18	0.58	7.08	0.86
5.7	7.35	0.88	24.77	2.52
2.8	3.21	0.58	13.83	1.47
1.4	4.99	0.70	17.79	1.84
0.85	5.78	2.13	33.69	3.40
0.57	10.82	1.19	-	

4. Conclusions

Ammonium tartrate dosimeters have features in common with alanine; both are of complex EPR spectra despite the simple appearance of the ammonium tartrate spectrum, both have complex time dependence, and both of them possess tissue equivalency and linear responses over a very wide range of radiation doses. However, ammonium tartrate showed more sensitivity toward radiation doses than did alanine dosimeters; their sensitivity was much better than that of alanine by a factor ranging from 1.84 to 2.1 times. The ammonium tartrate showed better percentage precision and lower values of associated combined uncertainties compared to the alanine. Based on the current study and also previous studies, ammonium tartrate can replace and be used side-by-side with alanine in many radiation dosimetry applications.

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