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## **Ammonium Dithionate – a New Material for Highly Sensitive EPR Dosimetry**

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## **Abstract**

Polycrystalline ammonium dithionate has been examined for its radiation response in the low dose range (< 5 Gy) using EPR technique. The  $\bullet\text{SO}_3^-$  radical ion was detected as a single EPR line with a peak-to-peak derivative width of *ca.* 0.44 mT in irradiated samples and its intensity was found to vary linearly with dose. At equal and moderate settings of microwave power and modulation amplitude ammonium dithionate was at least 7 times more sensitive than L-alanine which is the most common EPR dosimeter standard. Pulse experiments were performed on the powder samples to obtain the longitudinal relaxation time. These and microwave saturation experiments served to indicate the optimal microwave power to be applied during measurements as an EPR dosimeter for best sensitivity of this material. It is thus claimed that ammonium dithionate has excellent potential to become an EPR dosimeter with a low limit of the measurable dose for cases where tissue equivalence is not required or can be corrected for.

## Introduction

During the latest two decades EPR dosimetry has made considerable progress in a wide variety of applications ranging from radiation sterilization to radiation therapy.[1,2] For high radiation dose L- $\alpha$ -alanine has been successfully applied. Efforts to measure lower doses have been made, and a dose range of 1 -  $10^5$  Gy for the alanine dosimeter has been reported [3].

Although the sensitivity of this material has been much improved, there is still a need for more sensitive materials to routinely determine doses in the range below 5 Gy of clinical interest, however [4-6]. For this reason a current interest is focused on the engineering of new materials for better radiation response, with a view to using them for clinical applications. This necessitates the development of materials which can yield stable center having intense, preferably structureless EPR lines.

Some approaches relevant to the development of materials for EPR dosimetry have recently been discussed. A series of organic materials have been screened partly in our own work on for example ammonium tartrate  $((\text{NH}_4)_2\text{C}_2\text{H}_4\text{O}_6)$  [7-10], ammonium formate  $(\text{NH}_4\text{OOCH})$  [11], and lithium formate  $(\text{LiOOCH}\cdot\text{H}_2\text{O})$  [12-15].

Bogushevich and Ugolev [16] have discussed some aspects of inorganic EPR dosimeters for medical radiotherapy and have shown that alkaline earth dithionates have great potential. Irradiated dithionates exhibits a single, narrow line stable at room temperature attributed to  $\bullet\text{SO}_3^-$  radical anions.

Recently we have discussed some experimental approaches relevant to development of such EPR materials. We have demonstrated that polycrystalline dithionates and formates are promising

materials for EPR dosimetry, giving a large yield of radiation induced stable radicals. Both compounds have shown linear dose response in the range of clinical applications.  $^6\text{Li}$ , enriched and  $^7\text{Li}$  in natural composition of Li offer a possibility to measure the absorbed dose from photons and thermal neutrons. The signal for photon irradiation is increased two-fold by employing  $^6\text{Li}$  instead of Li with natural composition. This exchange decreases the line width and affects the peak-to-peak intensity; however the integrated intensity remains the same in both examined materials. A spectrum due to the  $\bullet\text{SO}_3^-$  radical anion was observed after irradiation of lithium dithionate. Studies with low energy X-ray irradiation showed that the signal amplitude increased using the  $^6\text{Li}$  in place of the Li with natural composition of isotopes. Due to the decreased line width, caused by the difference in  $g_N$  and  $I$  between the isotopes, the sensitivity with  $^6\text{Li}$  dithionate may be enhanced by an order of magnitude compared to alanine dosimetry. Interesting properties of the radical formation might be visible due to the large difference in ionization density of neutrons compared to photons.[17]

A distinct advantage of dithionates compared to the alanine dosimeter, and even to the formates is its narrow intense single line EPR spectrum resulting in an increasing sensitivity. In this note we present the results on pure ammonium dithionate as a potential candidate for highly sensitive EPR dosimetry.

## **Experimental**

### **Preparation of Ammonium Dithionate**

Polycrystalline samples of ammonium dithionate were prepared from manganese dithionate. An aqueous solution of manganese dithionate was treated with an excess quantity of  $(\text{NH}_4)_2\text{CO}_3$  added as an aqueous solution over about 1 hour with stirring. Stirring was maintained for about 2 hours and then the white suspension was filtered. The clear ammonium dithionate solution was evaporated *in-vacuo* to yield solid ammonium dithionate as a white crystalline material.

100 mg of the polycrystalline ammonium dithionate was pressed to pellets/tablets with a diameter 4.5 mm and height 4 mm. A small amount of liquid paraffin was added as binder and also as protection layer against absorption of water. L- $\alpha$ -alanine pellets prepared in a similar way were used as a reference material.

For dose-response comparison both materials – ammonium dithionate and L- $\alpha$ -alanine were irradiated with 4 MV X-rays from a Medical Varian Linac to well defined absorbed doses in the region 1-5 Gy. Irradiation with low energy X-rays was carried out with a PW1730 unit from Philips operated at 70 kV.

## **EPR measurements**

The continuous wave (CW) measurements were carried out with a Bruker ER 200D-SRC spectrometer operating at the X-band and equipped with an ESP 1600 computer. The signal intensity was measured as the peak-to-peak amplitude of the first derivative of the absorption spectrum. To correct for variation in spectrometer sensitivity, a reference sample of MgO containing Mn(II) was measured simultaneously. The six sharp lines of Mn(II) do not interfere with the signal of ammonium dithionate. The sample position and Mn<sup>2+</sup>/MgO reference position remained the same in all measurements, as described in detail elsewhere [11].

In order to study the saturation properties of the ammonium dithionate the microwave power was varied between 0.1 and 100 mW with modulation amplitude of 0.1 mT. The modulation frequency used was 100 kHz.

Pulse EPR measurements were made by means of a Bruker Eleksys 580 FT/CW X-band spectrometer equipped with a Bruker EN4118X-MD4-W1 dielectric resonator and the Bruker Eleksys software. For the pulsed EPR experiments powdered samples were placed in 3 mm outer diameter fused Suprasil quartz tubes and irradiated at room temperature with low energy X-rays. To find the longitudinal relaxation time inversion recovery experiments were performed. The pulse sequence was  $[\pi-\tau-\pi/2-T-\pi-T-echo]$  in which  $\tau$  was varied while the time between the end of the second pulse and the beginning of the third pulse was held constant at  $T = 200$  ns. A  $\pi$  pulse was 32-long. All experiments with CW and pulsed EPR were performed at room temperature.

## Results and Discussion

No detectable signal was observed in any of the samples before irradiation. The results were obtained with the same spectrometer settings for all investigated samples. The EPR spectrum of ammonium dithionate after irradiation by 4MV X-rays is shown in Figure 1. For comparison the EPR spectrum of L- $\alpha$ -alanine irradiated with the same dose and recorded with the same conditions/spectrometer settings is attached. In most of the previously investigated dithionates the EPR spectrum consisted of a single structureless line. In  $\text{Cs}_2\text{S}_2\text{O}_7$ , however, hyperfine structure from  $^{133}\text{Cs}$  was observed and assigned to the trapped  $\text{Cs}^+ \dots \text{SO}_3^-$  complex [18,19]. The hyperfine coupling to the protons and/or the nitrogen of the ammonium group is not resolved in the EPR spectrum of ammonium dithionate.

The spectrum in Figure 1 is accordingly assigned to the  $\bullet\text{SO}_3^-$  anion radical exhibiting a typical signal observed in other polycrystalline materials. This signal is stable at room temperature [17]. The  $\bullet\text{SO}_3^-$  peak-to-peak line width of ca. 0.44 mT in ammonium dithionate was lower than that of 0.675 mT observed for lithium dithionate, and would result in an increased sensitivity by  $(0.675/0.44)^2 = 2.35$  if all other factors were equal. As shown in Figure 1 the signal intensity measured peak-to-peak of  $\bullet\text{SO}_3^-$  anion radicals is much higher than L- $\alpha$ -alanine irradiated with the same dose.

The signal intensity as a function of absorbed dose for samples irradiated with doses of 1, 3 and 5 Gy is shown in Figure 2. As a reference the alanine sample were irradiated with the same dose

as the dithionate. As shown in Figure 2 the sensitivity of ammonium dithionate of about seven times that of alanine is also apparent from the slopes of the dose response curves.

A short spin-lattice relaxation time is preferred for a sensitive dosimeter material since it is possible to increase the microwave power without saturating the signal. Figure 3 shows that the signal recovery measured at room temperature using the spin echo detected inversion recovery method is slower for  $\bullet\text{SO}_3^-$  ( $T_1 = 35 \cdot 10^{-6}$  s) in ammonium dithionate than it is for the L- $\alpha$ -alanine radical ( $T_1 = 2.8 \cdot 10^{-6}$  s), indicating that the  $\bullet\text{SO}_3^-$  radical is more easily saturated by microwave power than the alanine radical. This was confirmed by the CW ESR measurements in Figure 4 giving the signal intensity (peak-to-peak) as function of microwave power. It can be seen that the signal gets saturated in ammonium dithionate around 1.8 mW.

## Conclusions

Ammonium dithionate has been investigated as a potential dosimeter material. The radical signal in irradiated polycrystalline samples is a structureless narrow line. Ammonium dithionate was found to be more sensitive than L- $\alpha$ -alanine by a factor of seven at the same spectrometer settings. The results indicate that the ammonium dithionate can be applied as a dosimeter for situations when a material more sensitive than L- $\alpha$ -alanine is needed.

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**Figures captions:**

**Fig. 1.** EPR signals obtained at the same spectrometer settings (microwave power of 2 mW and modulation amplitude of 0.1 mT) for ammonium dithionate and l-alanine after irradiation by 4MV X-rays.

**Fig. 2.** ESR derivative peak-to-peak signal intensity as a function of absorbed dose after irradiation with 4MV X-rays for the same spectrometer settings for ammonium dithionate and l-alanine

**Fig. 3.** Spin-lattice relaxation times,  $T_1$ , measured at room temperature using spin echo detected inversion recovery method for the same spectrometer settings for ammonium dithionate and l- $\alpha$ -alanine.

**Fig. 4.** CW ESR microwave power saturation measurements giving the signal intensity (peak-to-peak) as function of microwave power.

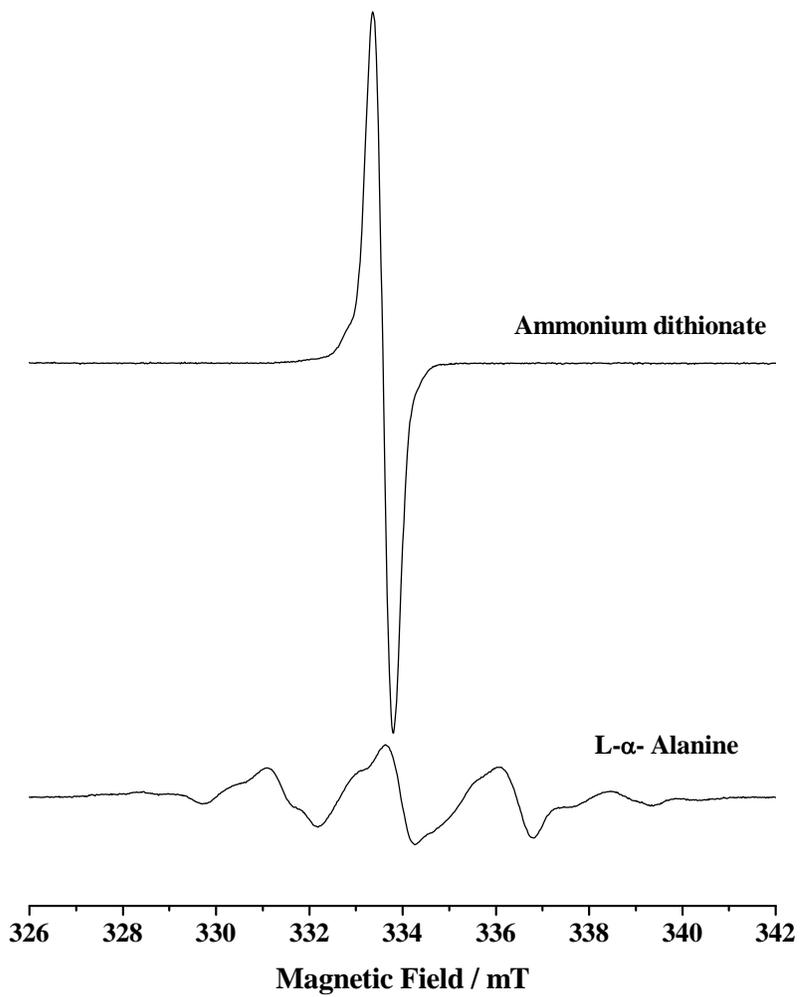


Fig. 1.

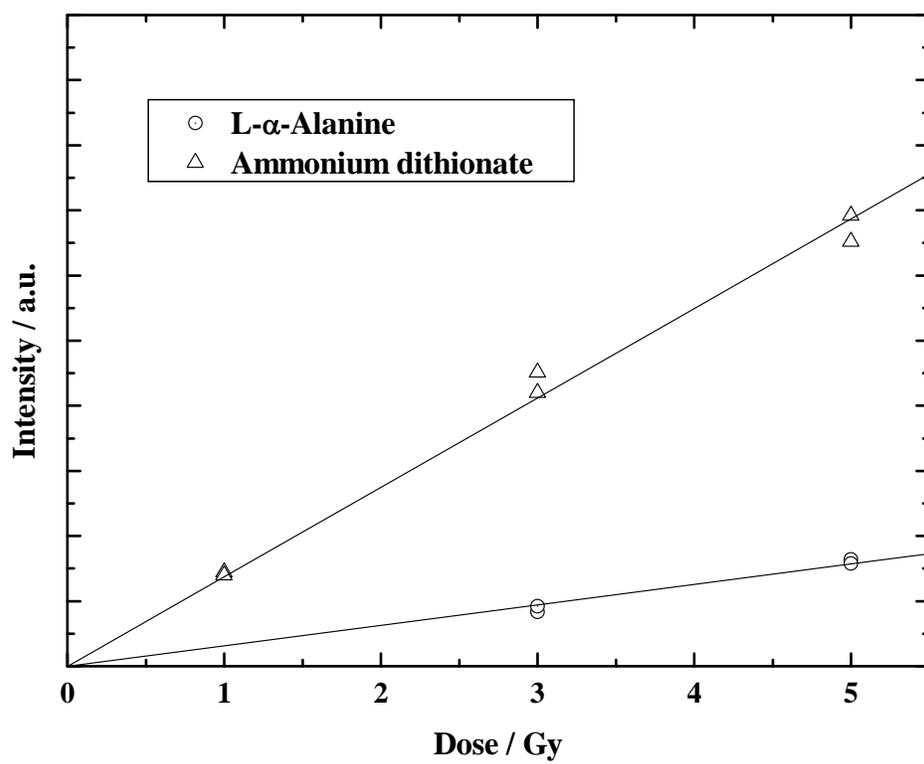


Fig. 2

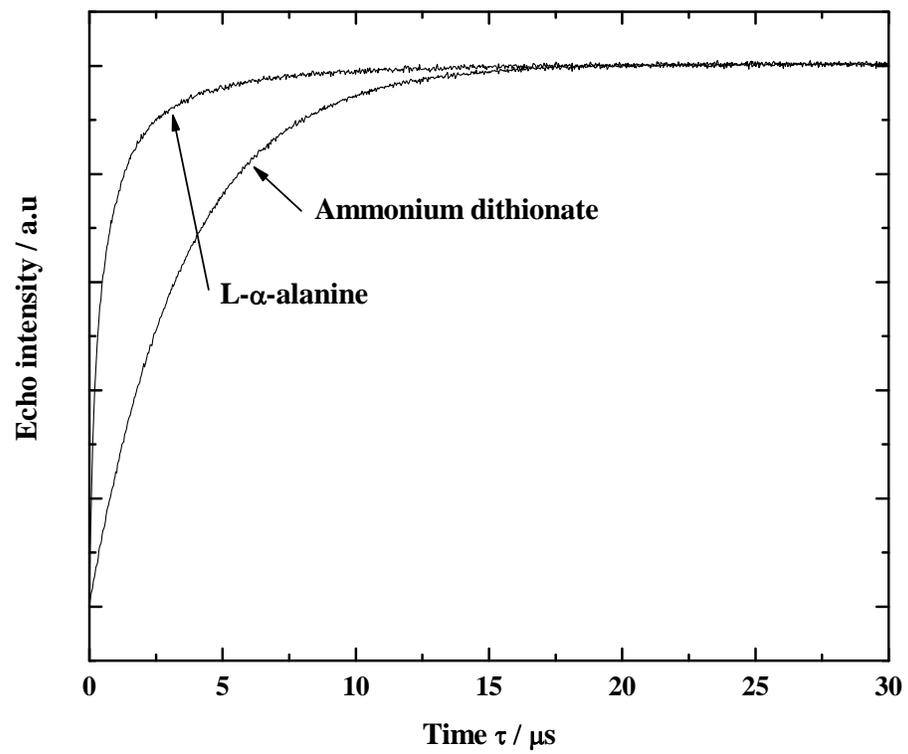


Fig. 3

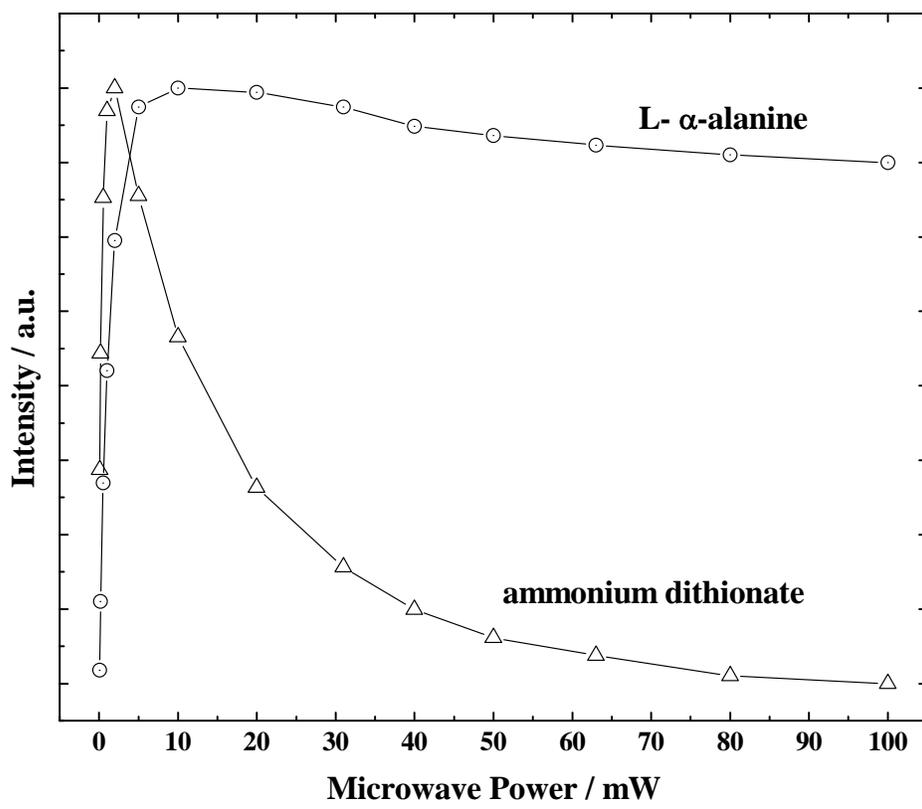


Fig. 4