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# Study of the ESR signal of gamma irradiated hydroxyapatite for dose assessment

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**Abstract**

In this work the ESR signal based on the measurement of the concentration of radiation induced radicals $CO_2^-$ in hydroxyapatite, obtained from human tooth enamel, was investigated aiming to standardise the sample preparation method and the measurement conditions for practical application of this technique to accident personal dosimetry. In this regard, practical considerations of sample preparation, grain size, ESR spectrum, spurious induced mechanical ESR signal, influence of dose radiation and measurement temperatures are discussed, as well are presented results of signal reproducibility, angular and microwave power signal dependence.


*Keywords:* Accident dosimetry; Tooth enamel; Dosimetry; ESR; Hydroxyapatite

## 1. Introduction

Ionising radiation produces free electrons, some of which may be trapped by impurities or by defects in solids. Some of the produced defects are stable with time and are measurable by electron spin resonance (ESR). The information obtained based on ESR spectroscopy has been extensively used to characterise the paramagnetic centres created by ionising radiation in alanine, sugar, calcium carbonate and hydroxyapatite present in tooth enamel and bones [1–4,7,9,10].

In this work it is studied the method based on the measurement of the concentration of radiation induced radicals $CO_2^-$ in hydroxyapatite, aiming to standardise the sample preparation method and the measurement conditions for practical application of this technique to accident personal dosimetry.

## 2. Material and methods

The samples were prepared in the following steps [6,7,13,14]: (1) the roots of the teeth were cut off using a diamond saw with water irrigation; (2) the enamel was separated mechanically from the dentine with a dental drill; (3) some samples were cut in slabs (about 500 μm thick) and others were crushed manually to obtain powder with grain sizes between 80 and 200 μm.

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The obtained ESR spectrum of non-irradiated samples present a mechanical induced signal with $g = 2.0039 \pm 0.0003$, different from radiation induced signal with $g_{\|} = 1.9973$; $g_{\perp} = 2.0022$. This signal is thermally stable, has no fading and is not affected by the radiation dose, but its amplitude depends on the grain size. It was not performed any chemical or thermal treatment to reduce organic compounds.

The samples were always irradiated with $^{60}$Co-gamma rays (at room or liquid nitrogen temperature) under electronic equilibrium conditions and placed in quartz ESR sample tubes. All dosimetry calibrations performed were carried out in the known radiation field of the Radiation Technology Centre – CTR from IPEN. The samples were stored in a controlled environment with low relative humidity, aiming to eliminate transient signals.

The ESR measurements were performed using a conventional X band spectrometer Bruker-EMX (Bruker Instruments, Billerica, MA) with a standard rectangular cavity (model ER4102ST) of the Physical Institute – USP. The parameters of measurement are shown in Table 1.

The first derivative of the actual absorption spectrum is displayed and the peak-to-peak amplitude values of the radiogenic signal are recorded for relative dose measurements and are based on linear dose dependence. The assessment of the absorbed dose can be done by the additive method or by the dose response curve [10,11,14]. In this work it was used the dose response curve method for dose reconstruction because it is a non-destructive fast method and the variation of radiation sensitivy of enamel is independent of the applied dose evaluation method. The parameters of the calibration curve, slope and intercept with dose axis were determined by linear regression analysis.

At lower doses it is necessary to subtract the broad radiation insensitive signal from the total spectrum or to use the selective saturation method, which is based on the fact that above a certain level of microwave power the intensity of the dosimetric signal increases with power, while the intensity of the native background signal saturates [8,10].

Contributions of medical X-ray examinations to enamel dose were not studied, but knowing that additional research is necessary in this field.

## 3. Results

Fig. 1 shows the first derivative of the paramagnetic absorption spectrum of a slab of tooth enamel irradiated (100 Gy) and recorded at room temperature. There are mainly two components contributing to the ESR signal. The induced radiation signal has an anisotropic $g$-value ($g_{\|} = 1.9973$; $g_{\perp} = 2.0022$) and is attributed mainly to $CO_2^-$ radicals, at present, it is not clear whether the species are indeed axial or orthorhombic [9]. Some woks show the majority of ESR signal radiation induced in tooth enamel are carbonate derived, i.e. $CO_2^-$, $CO_3^-$, $CO^-$, $CO_3^{3-}$, but also radicals derived from phosphate, i.e. $PO_4^{2-}$, and oxygen, i.e. $O^-$ and $O_3^-$ were identified [9,10].

The signal marked with asterisk in the spectrum of enamel slab is not exactly explained; it doesn't appear in annealed samples, and may be due to organic radicals presents in the sample. It is very likely that this native signal originated from several different groups of radicals located in different sites.

Table 1
Typical settings of ESR spectrometer parameters

| Magnetic field parameters | Microwave parameters | Signal channel parameters |
|---|---|---|
| Centre field: ≈350 mT | Microwave frequency: ≈9.8 GHz | Modulation frequency: 100 kHz |
| Sweep width: 2–10 mT | Microwave power: 1–40 mW | Modulation amplitude: 0.1–5 mT |
| Time of sweep: variable | | Conversion time: 20 ms |
| Resolution: 4096 points | | Time constant: 80 ms |
| | | Number of scans: 1–100 |

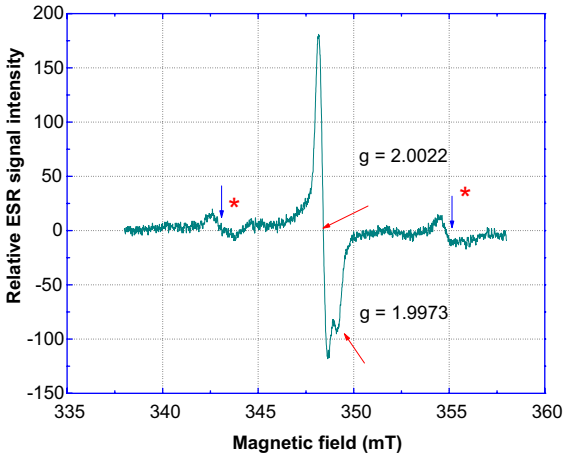


Fig. 1. First derivative of the absorption curve (arbitrary units) of slab tooth enamel irradiated with $^{60}$Co gamma rays (100 Gy) at room temperature with respect to the applied magnetic field (mT).

Fig. 2 shows the results obtained for powder samples of tooth enamel irradiated (100 Gy) and differs from the spectra of slab enamel.

The changes of the ESR signal in irradiated tooth enamel piece as a function of the direction of the static magnetic field due to the crystalline structure of tooth enamel is showed in Fig. 3 for angles between 0° and 100°. The intensities of the

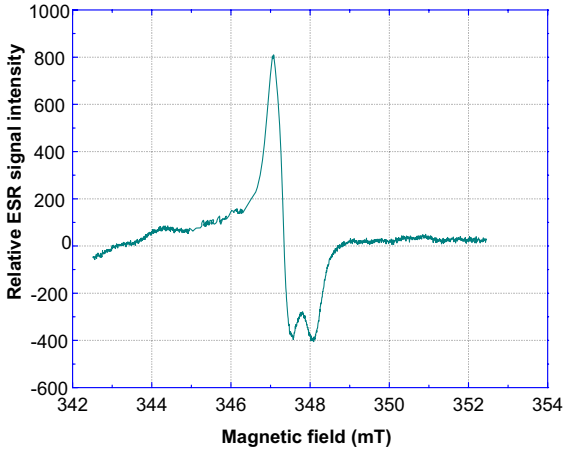


Fig. 2. First derivative of the absorption curve (arbitrary units) of powder tooth enamel irradiated with $^{60}$Co gamma rays (100 Gy) at room temperature with respect to the applied magnetic field (mT).

$g$-value will depend on the orientation of the crystal with respect to the external field and can vary 50%. To eliminate the angular dependence of the ESR signal the samples are used in powder form [1,4,12].

The ESR response at low temperature was investigated using powder samples irradiated (3.3 kGy) and read at 77 K immediately after irradiation, aiming to observe the signal evolution for to choose the signal to be used in accidental dosimetry. The obtained spectrum is shown in Fig. 4. This spectrum differs from that observed when the sample is irradiated and read at room temperature. These species are very stable at 77 K, and no significant decrease in the signal intensities was observed when the samples were kept at 77 K during several days.

In the case were the sample was irradiated at 77 K (5.2 kGy) and the measuring temperature was gradually increased, the ESR spectrum presented small changes due to recombination process. The obtained results showed that increasing the reading temperature from 77 K to 300 K the signal intensity decreases 70%. These changes in the signal amplitude were measured in a powder sample and the signal amplitude was plotted against temperature and the results are shown in Fig. 5.

The logarithmic decay of the centres implies that the amplitude decay is inversely proportional to temperature. The amplitude of the signal plotted against $1/T$ is shown in Fig. 6. The plot is linear within the experimental uncertainties and indicates which the defects annihilate each other when the temperature arises [4,5].

The influence of microwave power on the ESR signal intensity was investigated. The ESR response of samples presents an increasing amplitude that saturates at 20 mW. This study aimed to found the microwave power where the non-radiation induced ESR is partially saturated allowing easier measurement of radiation signal. Considering the result all measurements were performed using 10 mW microwave power.

The influence of post-irradiation storage on the radiation ESR response of the enamel was investigated. The samples were measured immediately after irradiation at room temperature and

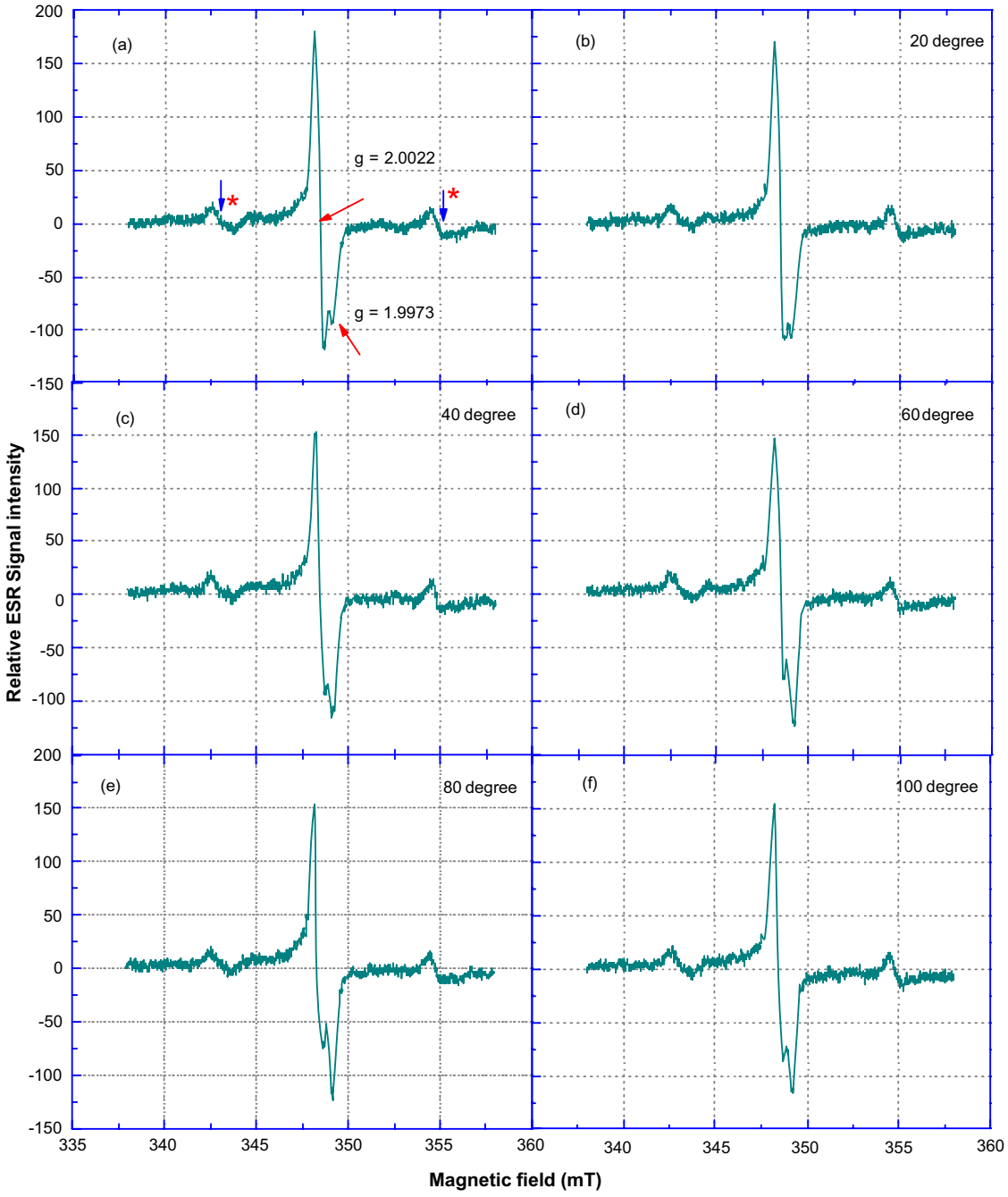


Fig. 3. Angular dependence of the ESR signal of slab enamel irradiated with $^{60}$Co gamma rays (100 Gy) at room temperature. (a) 0°; (b) 20°; (c) 40°; (d) 60°; (e) 80°; (f) 100°.

subsequently measured each 1-h during 14 h. The post-irradiation fading resulted in not-significant 2% decay of the signal amplitude, which stabilised within 12 h after irradiation, and the intensity

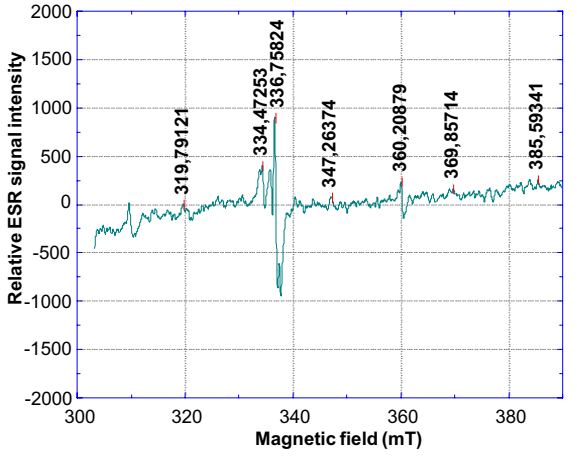


Fig. 4. First derivative of the absorption curve (arbitrary units) of powder tooth enamel irradiated with $^{60}$Co gamma rays (3.3 kGy) at 77 K with respect to the applied magnetic field (mT).

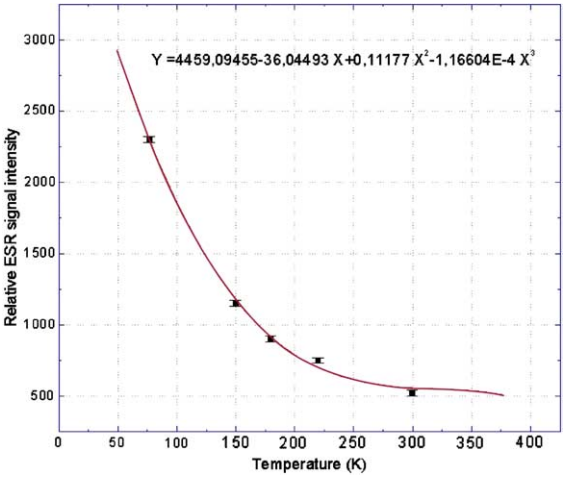


Fig. 5. Dependence of the ESR signal amplitude of powder sample as a function of observing temperature (77–300 K). Samples of tooth enamel irradiated with $^{60}$Co gamma rays (5.2 kGy) at 77 K in vacuum and read in temperature range of 77–300 K.

approached a constant. Therefore, all the ESR measurements were performed more than 12 h after the irradiation.

The dose dependence of the signal amplitude was found to be linear with an additive constant equivalent to the background amplitude as measured from non-irradiated samples. The obtained

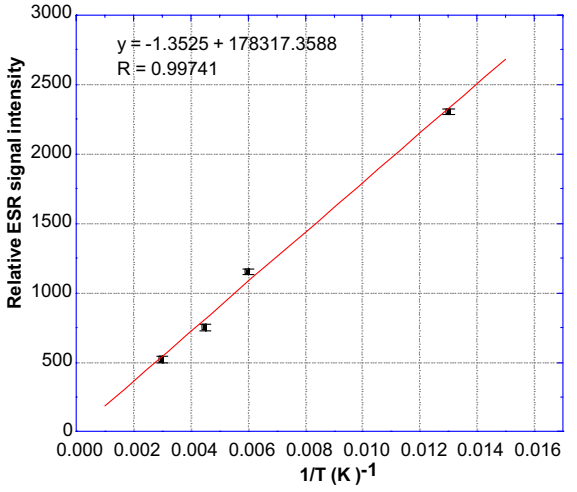


Fig. 6. ESR signal amplitude of powder samples irradiated with $^{60}$Co gamma rays (5.2 kGy) at 77 K in vacuum and read at temperature range of 77–300 K as a function of $1/T$.

results are shown in Fig. 7. The non-radiation induced ESR background signal was obtained from a sample, knowing that the sample had zero previous dose. An empty ESR tube spectrum taken at the time of sample measurement is subtracted, and separate spectra are obtained for each set of measurement parameters for which the standard will be used.

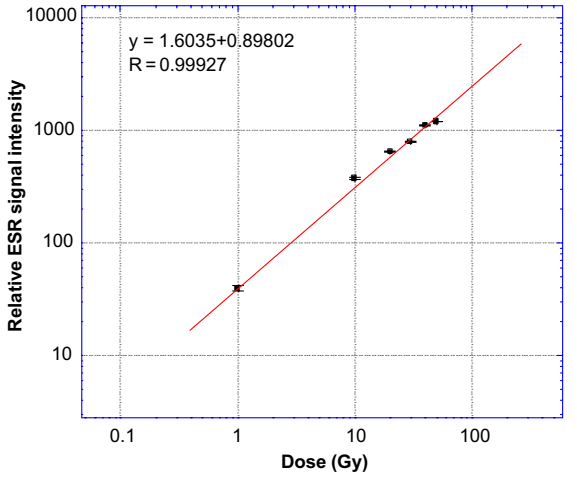


Fig. 7. Dose response curve of powder tooth enamel irradiated with gamma rays of $^{60}$Co at room temperature.

## 4. Conclusions

Experiments confirmed that tooth enamel can be used as a dosimeter for gamma radiation accident dosimetry and accidental doses of individuals can be derived from teeth samples.

The obtained results shown the importance of this joint effort the unifying, improvements and innovations of different techniques employed by various laboratories throughout the word for a standardise ESR tooth dosimetry.

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