NMR study of Fe^{3+} ions diffusion in gamma irradiated Fricke gel

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Abstract: A tube containing Fricke Xylenol Gel was partially shielded and irradiated with gamma radiation to assure that the NMR relaxation time has two components. The two parts were measured and an inversion-recovery sequence was used to obtain the signal from different parts selectively. The dispersion in spatial radiation distribution as well as the apparent diffusion coefficient of Fe^{3+} through the sample was measured using the NMR spectra of the sample located in a z gradient.

Keywords: 3D dosimetry, Fricke-infused gel dosimeter, spatial dose information, Magnetic Resonance Spectroscopy (MRS), iron ion diffusion coefficients.

INTRODUCTION

Cancer treatment planning is a very important practice for modern conformal radiotherapy techniques such as IMRT (Intensity Modulated Radiation Therapy), Stereotactic Radiosurgery and HDR (High Dose Rate) Brachytherapy. These techniques require knowledge of a three dimensional (3D) dose distribution.

Among the recent techniques devoted to evaluate 3D dose distribution, the Fricke-infused gel dosimeter (Gore et al, 1984; Bero et al, 2001) has been largely studied, it combines basic gel dosimeter principle (Ibbott, 2004) with well established Fricke dosimeter (Fricke et al, 1966). The main advantage to perform radiation measurements using gel dosimeters is that it is possible to obtain spatial dose information by imaging the radiation induced chemical changes using techniques sensitive to physical changes, for instance, the Nuclear Magnetic Resonance (NMR) relaxation characteristics (Rabbani et al, 1983) can be evaluated by means of Magnetic Resonance Imaging (MRI). The image intensity can offer information about the concentration of Fe^{+3} ions throughout a phantom and can be analyzed to give the spatial dose information. Preliminary results of 3D dose distribution evaluation carried out in the NMR laboratory of Sao Paulo University using breast and head phantoms filled with FXG solutions prepared at IPEN with 270 Bloom gelatin, irradiated with ^{60}Co radiotherapy source and gamma knife system respectively, indicate that this technique can be successfully used and the percentage dose distribution curves well established (Galante et al, 2007; Cervantes et al, 2008).

To improve the 3D dose distribution evaluation the diffusion of ferric ions has to be very well established and characterized by measurements of the iron ions diffusion coefficients. The Fe^{3+} ions diffusion coefficients of different Fricke gel solutions are dependent on the parameters such as: gel type and concentration, irradiation, temperatures and other properties of the dosimeter (Schreiner, 2004; Chu, 2001).

Aiming to study the apparent diffusion of ferric ions in a Fricke Xylenol Gel solution (FXG) irradiated with ^{60}Co gamma radiation and using a High Resolution NMR spectrometer, a tube containing FXG solution was partially shielded and irradiated with gamma radiation to assure that the NMR relaxation time has two components. The two parts were measured and an inversion-recovery sequence was used to obtain the signal from different parts selectively. The dispersion in spatial radiation distribution as well as the apparent diffusion coefficient of Fe^{3+} through the sample was measured using the NMR spectra of the sample located in a z gradient.

MATERIALS AND METHODS

Fricke Gel Solution – FXG

The Fricke xylenol gel solution studied (pH 1.42 at 24.7° C; obtained using a pH-meter PHTEK model PHS-3B) was prepared using 5% by weight 270 Bloom porcine gelatin, tri-distilled water, 50 mM sulfuric acid (H_2SO_4), 1 mM sodium chloride (NaCl), 1 mM ferrous ammonium sulfate or Mohr salt [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$], and 0.1 mM ion indicator xylenol orange ($C_{31}H_{28}N_2Na_4O_{13}S$) (Olsson et al, 1989). After preparation were added two deuterium drops/1 mL solution in order to make possible the locking of Larmor frequency in the NMR measurements.

The obtained solution was conditioned in two glass tubes (5 mm diameter, 1 mm thick wall, 200 mm high) empty 40 mm (Fig. 1A) and maintained under refrigeration (4° C ± 1° C) and light protected during 18 h (sample that would be totally irradiated) and 40 h before irradiation (sample that would be partially irradiated). The first sample was measured by NMR spectroscopy technique 16 h after preparation.

Irradiation

Thirty minutes before irradiation the samples were removed from the refrigerator and maintained at room temperature. The irradiations were performed in free air using a ^{60}Co gamma radiation source at Radiation Technology Center of IPEN. Two samples were irradiated with absorbed dose of 50 Gy and dose rate of 89.8 Gy/h; in one of then the sample volume was totally irradiated (Fig. 1B) and in the other one the sample volume was partially irradiated (Fig. 1C). To perform the partial irradiations part of the solution volume was shielded using lead bricks (50 mm thickness each one) (Fig. 2). One lead brick was perforated in order to accommodate the glass tube filled with the dosimetric solution (Fig. 2C).

NMR measurements

The inversion-recovery sequence was used to measure the spin-lattice relaxation time, T_1, using a High Resolution NMR spectrometer *Varian* model *Gemini 2000* working at 200 MHz for protons. The spin-lattice relaxation time of non irradiated sample (Fig. 1A) called T_1^{2+} and irradiated sample (Fig. 1B) called T_1^{3+} were 868 ms and 404 ms, respectively. For the partially irradiated tube, (Fig. 1C), three different inversion-recovery sequences with different interval between 180 and 90 degree (t = 760, 310 and 5 000 ms) were used to acquire the NMR spectra, at the same time a linear gradient parallel to the main field, Z_1, was applied to codify the spatial distribution. These spectra were obtained in order to acquire the Z_1 profiles, the first t value, t = 760 ms, gives the longitudinal Fe^{3+} ions distribution, the second one gives the corresponding Fe^{2+} ions distribution and the last t = 5 000 ms value produce the typical Z_1 profile and was acquired to normalize and register, frequency offset correction of the profiles. The time evolution of the ions distributions were recorded by repeating those measurements half an hour, one hour, two hours and then every two hours approximately for 2 days. The time reference, $t = 0$, was the first resonance measurement after half hour of the partially irradiation. Fig. 3 shows the time evolution for the ferric ions and Fig. 4 shows the evolution of the ferrous ions.

RESULTS AND DISCUSSION

In Fig. 5 the experimental scheme is shown. The spatial coordinate is parallel to the tube axes and to the main field and varies between 0 and 1. The bottom, lower z position, was shielded to be protected from the irradiation while the top, high z position, was not shielded and therefore the irradiation process create Fe^{3+} ions. The frequency is proportional to the z coordinate due to the applied gradient. Fig. 3 shows the Fe^{3+} profiles acquired at different intervals of time. It can be seen that at low frequency values the signal amplitude is small, indicating a few amount of ferric ions which increases with time because the diffusion and oxidation process are taking place. At high frequency values the signal amplitude is great demonstrating a higher Fe^{3+} ion concentration which does not vary. Fig. 4 shows the ferrous ions profiles; the opposite behavior was observed because Fe^{2+} ions are in continuous oxidation process.

As it can be seen in Fig. 3, the first profile, took 30 minutes after the irradiation, ($t = 0$), resemble the initial dose distribution (Fig. 5). The second, third and fourth profiles was acquired half an hour, one hour and two hours respectively after the first measurement and are almost like the first one, preserving the absorbed dose distribution. The following profiles are significantly different. This ferric profile time evolution indicates that, in a FXG phantom, the absorbed dose is maintained almost for two hours and 30 minutes after the irradiation.

The apparent diffusion coefficient was obtained using the least-square fitting of the diffusion equation, the derivatives were substituted with the finite differences of profiles and the diffusion coefficient (2.5 x 10^{-1} cm²/h) was used as the fitting parameter which is closer to the one obtained by (Schulz et al, 1990).

The diffusion equation can be solved and fitted to the experimental Fe^{3+} profiles using least-square fitting with the global apparent diffusion coefficient as one parameter (Fig. 6A). The Fe total profile was used to fit the "hat" function in order to obtain the borders of the RF coil (Fig. 6B). Only the interval $0.5 < z < 1$ of the profile was fitted because the lateral artifact due to the B_1 coil gradient and tube susceptibility. In Fig. 7 the time dependence of the apparent diffusion coefficient obtained from curves of Fig. 6 is shown.

CONCLUSIONS

The method described in this paper permitted the acquisition of the one-dimension dose distribution in function of time; this distribution presents high precision in the space coordinate and good resolution in the time coordinate. Separated profiles for the ferric and ferrous ions can be obtained.

With these profiles it is possible to study the diffusion and oxidation of the sample and to extract the Fe^{3+} ions diffusion coefficient. For almost two hours and thirty minutes after starting the irradiation, the profile changes are small. Approximately two hours after irradiation, the ferrous oxidation process contributes more than the ferric ions diffusion to the apparent diffusion coefficient.

The method validates the use of FXG phantoms to obtain the three-dimensional absorbed dose distribution by MRI, almost 2 hours and 30 minutes after irradiation. The use of read gradient pulse can eliminate the artifact.

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Figure captions:

Figure 1 – Non-irradiated (A); irradiated (B); partially irradiated FXG solution (C).

Figure 2 – Experimental set up for partial irradiation of FXG solutions.

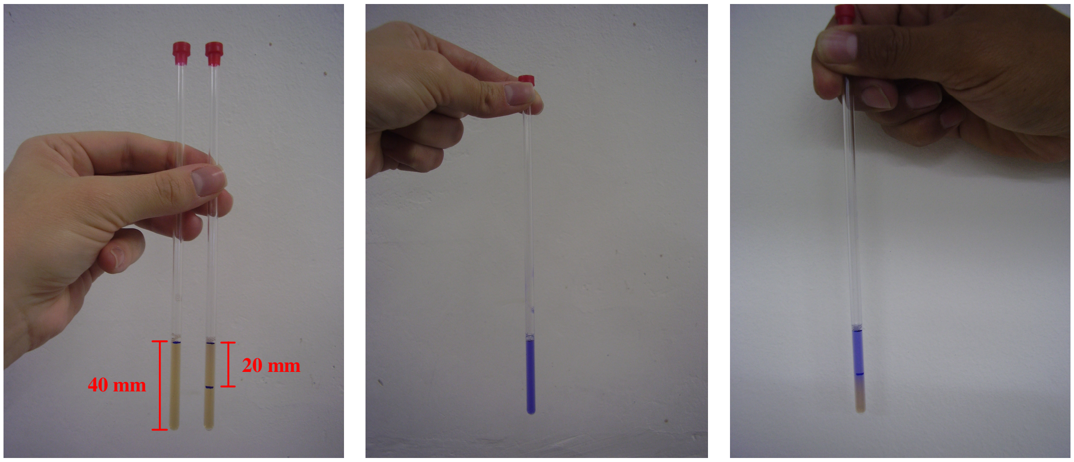
Figure 3 – Time evolution of the ferric ions profile. The time in this figure begins at the first measure, 30 minutes after the start of the irradiation.

Figure 4 – Time evolution of the ferrous ions profile. The time in this figure begins at the first measure, 30 minutes after the start of the irradiation.

Figure 5 – Schematic experimental setup.

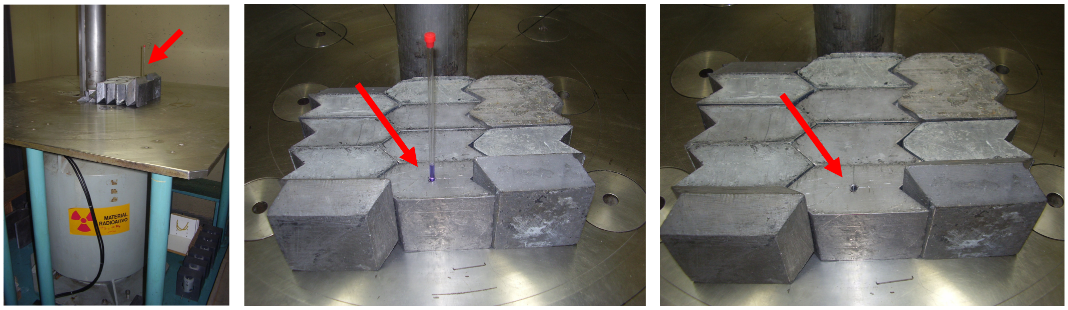
Figure 6 – Experimental curve fitting. Fe^{3+} profile fitted by the diffusion equation solution (A). The Fe total profile to obtain the coil's borders (B).

Figure 7 – Time dependence of apparent diffusion coefficient.



A B C

Fig. 1



A B C

Fig. 2

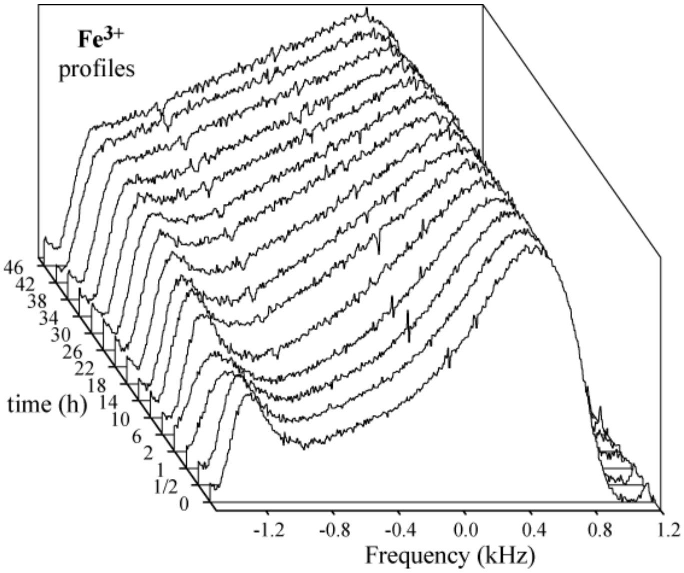

Fe^{3+}
profiles
time (h)
46
42
38
34
30
26
22
18
14
10
6
2
1
1/2
0
-1.2
-0.8
-0.4
0.0
0.4
0.8
1.2
Frequency (kHz)

Fig. 3

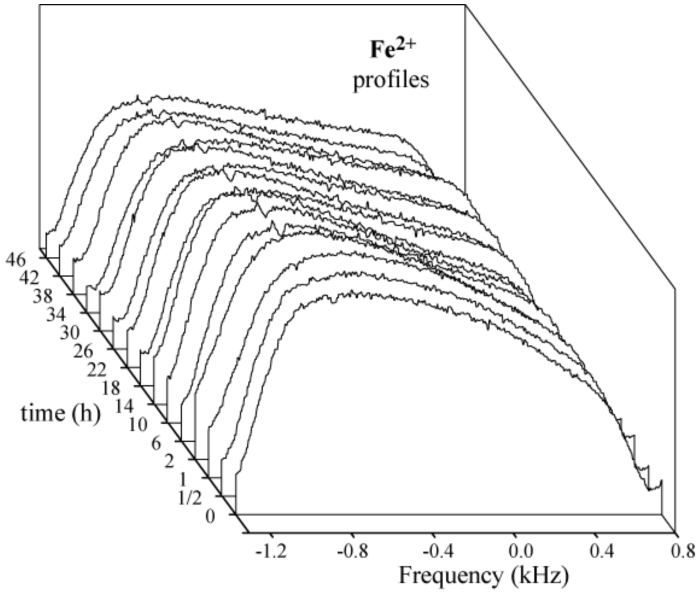
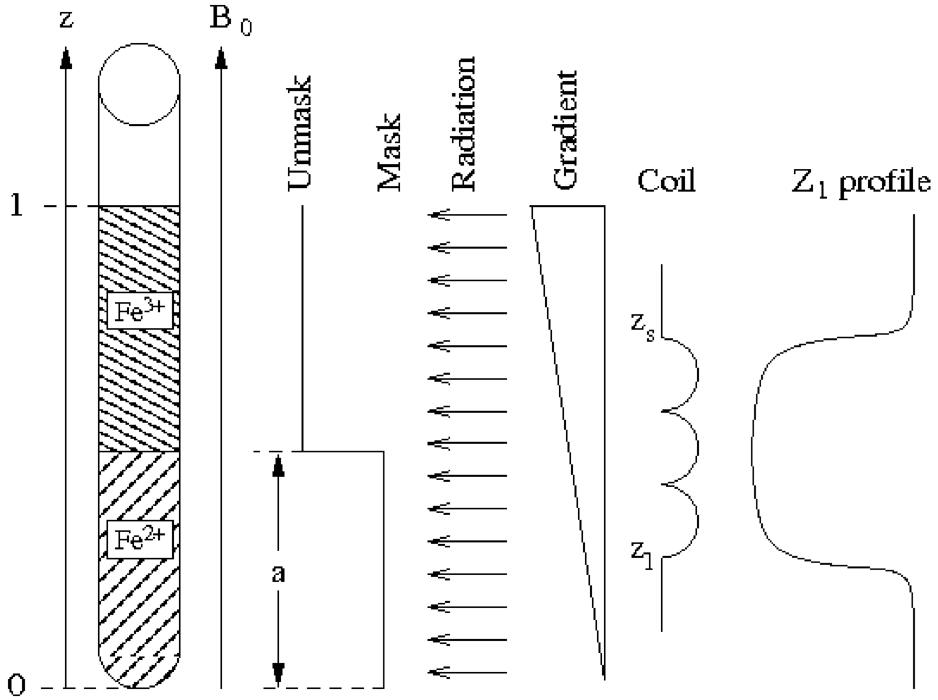

Fe^{2+}
profiles
time (h)
46
42
38
34
30
26
22
18
14
10
6
2
1
1/2
0
-1.2
-0.8
-0.4
0.0
0.4
0.8
Frequency (kHz)

Fig. 4


z
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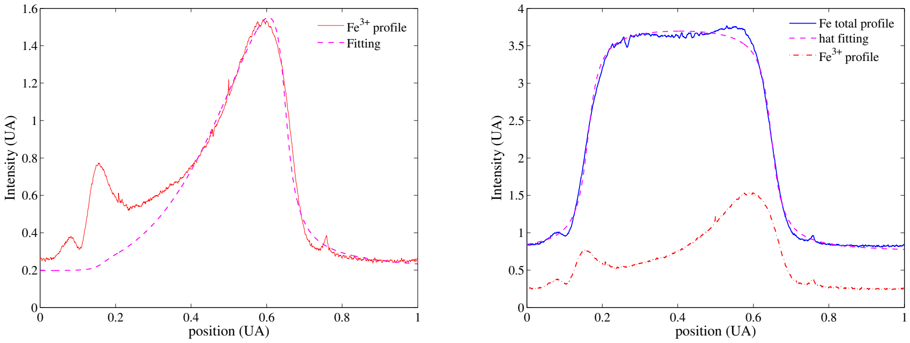
Fe3+
Fe2+
a
Unmask
Mask
Radiation
Gradient
Coil
zs
z1
Z1 profile

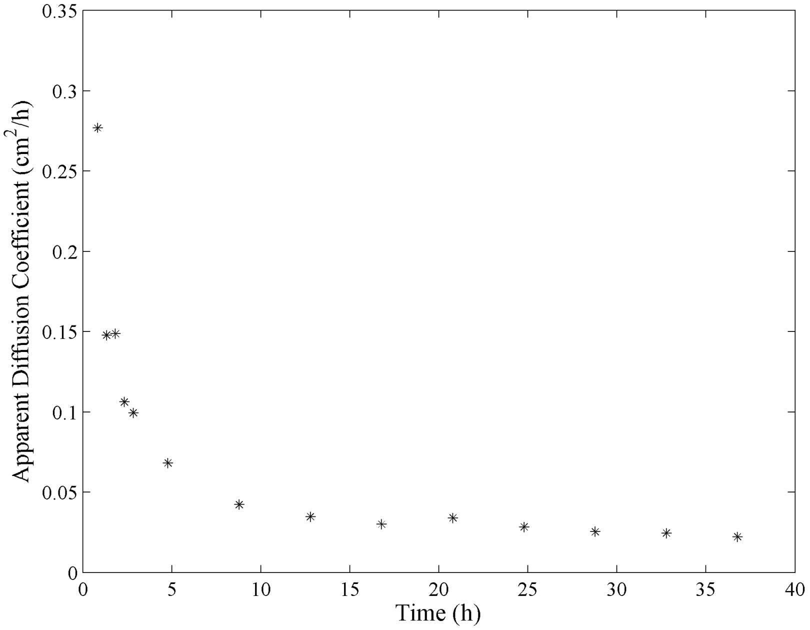
Fig. 5


Intensity (UA)
position (UA)
Fe^{3+} profile
Fitting
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Fe total profile
hat fitting
Fe^{3+} profile
0.5
1.5
2
2.5
3
3.5
4

A

B

Fig. 6


Apparent Diffusion Coefficient (cm^2/h)
Time (h)
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0.05
0.1
0.15
0.2
0.25
0.3
0.35
0
5
10
15
20
25
30
35
40

Fig. 7