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Abstract

The radiolysis mechanism of the Fricke-gel-dosimeters has been investigated in order to evaluate the role of hydrogels in the radical production. For this purpose, electron paramagnetic resonance (EPR) spectra were acquired for samples frozen and irradiated at 77 K. The analysis was performed by increasing stepwise the temperature and acquiring the EPR spectra at 120 K in order to follow the radical reaction mechanism. The comparison between aqueous- and gel- dosimeters were performed. Both gelatin from porcine skin and PVA (polyvinyl alcohol) were investigated as gel matrix.
Different radical species were identified and qualitatively compared. For gel matrix, peroxyl radicals, stemming from the hydrogel, play an important role in the survival of radicals at higher temperature. Moreover, the Fe3+ EPR signal has been studied and compared with the radicals concentration. From this comparison, it is evident the increase of Fe3+ concentration is shifted toward higher temperatures with respect to the radical decay. To explain this phenomenon, the intervention of EPR silent species like peroxides is supposed.

1. Introduction

The Fricke standard aqueous-dosimeter is an acidic solution of ferrous ions, Fe2+. Upon irradiation, the products of water radiolysis cause the dose-dependent oxidation of ferrous ions into ferric ions, Fe3+. A chelant, the Xylenol Orange (XO), is typically added in the dosimeter formulation to allow an optical measurement in the visible range. In details, the XO forms complexes with the ferric ions which mainly absorb at about 585 nm [Appleby and Leghrouz, 1991]. The spatial information of the absorbed dose is preserved by adding a gelling agent, viz. gelatin from porcine skin, agarose and polyvinyl alcohol (PVA) [Schreiner, 2004]. Olsson et al. (1991) reported an increase of the sensitivity of the gel-dosimeter due to a chain reaction in the agarose. Since the addition of organic compounds (e.g. sucrose) enhances the radiolytic yield of Fe3+, a similar effect is expected in the case of gelatin and PVA [Healy et al., 2003].
As the mass fraction of the gel component is usually less than 5%, the primary effect is the radiolysis of water. Therefore, the organic species stemming from hydrogels might play a key role in the reaction mechanism for the oxidation of iron. In this framework, the radicals are the most important species. The Electron Paramagnetic Resonance (EPR) technique is widely used for a qualitative and quantitative investigation of radicals. Thus, a systematic EPR analysis on both gelatin and PVA matrices was conducted in order to investigate the production and reaction of radicals with respect to the increase of Fe3+ concentration.
The radical reaction mechanism occurring at ambient temperature, i.e. in operative conditions, could be investigated by means of pulse radiolysis [Khaikin et al., 1996]. As an alternative, a previously developed methodology [Dondi et al., 2012] was applied using conventional EPR techniques. In details, samples were quickly frozen, irradiated and maintained at 77 K. Subsequently, samples were ana- lyzed in the EPR cavity at 120 K. The temperature was increased stepwise to allow the reactions between radicals and then quickly restored at 120 K for the measurement. Details of the adopted methodology and the obtained experimental results are hereafter discussed.

2. Materials and methods

Samples were prepared according to standardized procedures [Liosi et al., 2015; Xiao et al., 2010]. The chemical composition was: 0.5 mM ferrous ammonium sulphate (Sigma Aldrich F3754), 25 mM sulphuric acid (Carlo Erba Reagent, grade 96% pure) and 0.165 mM xylenol orange (Sigma Aldrich, 33825). When gel matrices are considered, 3% w/v gelatin from porcine skin (300 bloom gel strength, Sigma Aldrich, G2500) or 10% w/v PVA (Sigma Aldrich, 341584) crosslinked with 38.4 mM of glutaraldehyde (GTA) solution 25% w/w in water (Sigma Aldrich, G6257) were used.
To obtain frozen samples, 150 µL of each solution were pipetted in the conical holes (2.8 mm diameter x 3.5 mm diameter and 19 mm height) of aluminum cylinders. In the case of gel-dosimeters, this procedure was performed before the gelification. Afterwards, the holes were sealed using a plastic film. A rapid freezing of the solution was achieved by soaking the cylinders in liquid nitrogen. The frozen samples, 20 mm height, were removed from the cylinders and inserted in quartz tubes immersed in liquid nitrogen. The tubes were glass sealed by softening the top with a torch while keeping them under vacuum (rotary pump). During this procedure, the samples were maintained at liquid nitrogen temperature.
All the samples were irradiated at 2 kGy with gamma rays (60Co source, dose rate 0.14 kGy/h) at liquid nitrogen temperature (77 K). Results obtained in previous experimental campaigns show that 2 kGy is the minimum dose to obtain a detectable EPR signal for radicals.
According to a previously developed method [Dondi et al., 2012], the EPR spectra were recorded at 120 K and 10 mW with a field modulation amplitude of 1 G. The spectrometer was Bruker EMX-10/12 (Bruker BioSpin GmbH, Karlsruhe, Germany) operating in X-band and equipped with a ER4119HS cavity. The identification of both radical species and ferric ions was performed by gradually heating the samples inside the EPR cavity at different temperatures from 120 K to 300 K (the temperature was kept for 30 s), and restoring the measurement temperature (120 K) before each spectrum acquisition. The relative amount of organic radicals was measured by double integration of the EPR spectra. Instead, Fe^{3+} concentration was evaluated by computing the peak-to-peak value of the EPR signal at 1570G.

3. Results

The irradiation of frozen solution presents several advantages. In particular, the radicals formed are not free to move and thus to recombine. This opens the possibility to identify the primary radicals formed and to investigate radical reactions after annealing at higher temperatures. The dose (2 kGy) was chosen in order to ease the radical identification by EPR. Preliminary experiments at lower doses showed similarly results even if a quantitative evaluation was not possible.
The analysis of the EPR spectra recorded with samples obtained with solutions prepared with and without the xylenol orange did not show significant differences. For sake of brevity, only results for the solution including xylenol orange are hereafter reported.

3.1. Radicals

The EPR spectra for both PVA and gelatin matrices are reported in Fig. 1a) and b) respectively. As previously described, each spectrum was acquired after restoring the temperature to 120 K following the heating at different temperature.
During the investigation of both gel systems, several species of radicals were detected and identified at different temperature ranges (Fig. 1). In details, the first observed species were ·OH and ·OOH radicals [Bednarek et al. (1996), Pignatello et al. (2006)] trapped in the solid ice matrix. These unstable radicals disappeared leading to the formation of a mixture of carbon and oxygen radical species and secondly to the formation of peroxyl radicals ($g_{//}$=2.036, $g_{\perp}$=2.008). The quantitative evolution of the total amount of radicals with respect to the heating temperature (Fig. 2) showed some differences for Fricke dosimeter made with PVA, gelatin and in aqueous solution. A close look of the EPR spectra showed that, in the case of PVA, the radicals stemming from water quickly decreased from 120 K to 135 K. Then the secondary radicals remained stable up to 190 K with a yield of about 60%. Starting from this temperature peroxyl radicals survived up to 260 K.

In the case of gelatin, the radicals stemming from water survived up to 140 K when the secondary species appeared. The relative yield of formation, about 20%, was lower than in the case of PVA. Starting from 170 K a signal attributable to peroxyls was observed up to 240 K. It is worth to note that the low amount of the peroxyl radicals is difficult to quantify by the double integration of the EPR spectra.
For comparison, a similar procedure was performed on aqueous dosimeter. As in the case of gel dosimeters, hydroxyl radicals are the dominant species up to 140 K (Fig. 1c). At higher temperatures almost no signal is present (Fig. 2).

3.2. The ferric ions

The quantitative measurement of Fe^{3+} by EPR was made by considering the peak-to-peak value at g=4.3 [Karimova, 1981, Bou- Abdallah et al., 2008]. However, a broad peak occurring at g=2 affects the peak baseline and, as a consequence, the result. This effect might be due to electron-spin exchange interactions which depend on the size of microcrystalline regions. During the measurement thermal cycle these regions could undergo to change in size thus affecting the measurement [Karimova, 1981]. A preliminary measurement of a frozen solution of Fe^{3+}(0.15 mM) showed that the magnitude of the effect corresponds to a signal variation of about 0.05 a.u.
The comparison of the variation of the normalized Fe^{3+} concentration with respect to the temperature for aqueous, PVA and gelatin Fricke samples is shown in Fig. 3. In the case of irradiated PVA and gelatin, an increase of signal is visible after heating at 230 K, while for aqueous Fricke, the signal increases starting from 170 K.
After a comparison of the increase of Fe^{3+} EPR signal and decrease of radicals (Fig. 2) it is evident that the increase of iron is shifted toward higher temperatures, after the disappearance of most of radicals. Nevertheless, organic peroxyl radicals could give rise to hydrogen abstraction with the formation of hydroperoxides, that are EPR silent. These species could react at higher temperatures due to activation energies for the Fenton reaction and also to limited diffusion in the frozen matrix [Pignatello et al., 2006, Orr and Williams, 1952, Hardwick, 1956]. In the case of irradiated Fricke in water, ·OOH radicals could form hydrogen peroxide, that is more reactive with respect to hydroperoxides [Hardwick, 1956; Orr et al., 1952] and thus promote the iron oxidation at lower temperatures.

4. Discussion

Starting from the well-known difference in system sensitivity for Fricke aqueous- and gel-dosimeters [Olsson et al., 1991], a comparison was conducted via EPR technique with the aim to investigate the role of the hydrogel in the process of radicals production.
In particular, from the spectra acquired for Fricke-gel-dosimeter, it was possible to identify peroxyl radicals stemming from carbon back-bone of the hydrogels, which are not present within the aqueous dosimeter. We can suppose that during the heating, hydroxyl radicals reacts with hydrogels forming carbon and oxygen radicals. The latter, due to the oxygen diffusion can form peroxyl radicals that, due to their stability, remain up to 220 K.
On the basis of the experimental results, we can suppose the following reactions sequence in the case of gels:

$H_2O + \gamma \rightarrow HO^{\cdot} + HOO^{\cdot}$ (1)

$HO^{\cdot} + RH \rightarrow R^{\cdot}$ (2)

$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$ (3)

$ROO^{\cdot} + R'H \rightarrow ROOH + R'rad$ (4)

$ROOH + 2Fe^{2+} + 2H^{+} \rightarrow ROH + H_2O + 2Fe^{3+}$ (5)

[Pignatello et al., 2006].

For aqueous Fricke, instead, equations 2–5 are due only to organic impurities, and then the iron oxidation might follows the reaction:
$H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + H_2O + OH^{\cdot}$
Therefore, the oxidation of the ferrous ions could be mainly related to the presence of peroxide, even if, due to the irradiation of frozen solution at 77 K, no chain reaction can be observed as in the case of liquid solution [Olsson et al., 1991].

5. Conclusions

In this study we proposed EPR measurement of frozen solutions as an alternative to pulse radiolysis [Khaikin et al., 1996] for the study and the determination of radicals. Even with the known differences with the liquid phase, this technique could be useful for the determination of the relative radical stability and the evolution from radio- induced primary radicals up to secondary radicals can be investigated. One of the main differences of the proposed method with the liquid phase is the greater influence of diffusion of radical species in the solid matrix with respect to the liquid. In fact, in our conditions, the chain reactions are limited to some extent and the diffusion of species is reduced. This lead to an overall reduced sensitivity of the frozen dosimeter with respect to liquid. Nevertheless, we observed an enhancement of Fe^{3+} production in the gel dosimeter. This effect might be related to a higher efficiency in the radical transfer from water primary radicals to carbon radicals leading to peroxide radicals and then peroxides. In fact, unstable radicals produced by water radiolysis induce a damage on the polymer ending with more stable and thus less reactive species. In the case of an aqueous dosimeter, the reactive primary species would undergo mainly to coupling reactions. Even if a direct correlation between the disappearance of radicals and the increase of Fe^{3+} was not observed, it is reasonable to suppose the formation of peroxides and it is well known too that the latter species causes iron oxidation.
As a conclusion, the technique presented in this paper could be an alternative to pulse radiolysis coupled with kinetic spectrophotometry at least in terms of radical identification. Nevertheless, a deeper study on EPR silent molecular intermediates might be of fundamental importance for the elucidation of the reaction mechanisms in Fricke- gel dosimeters.

Acknowledgments

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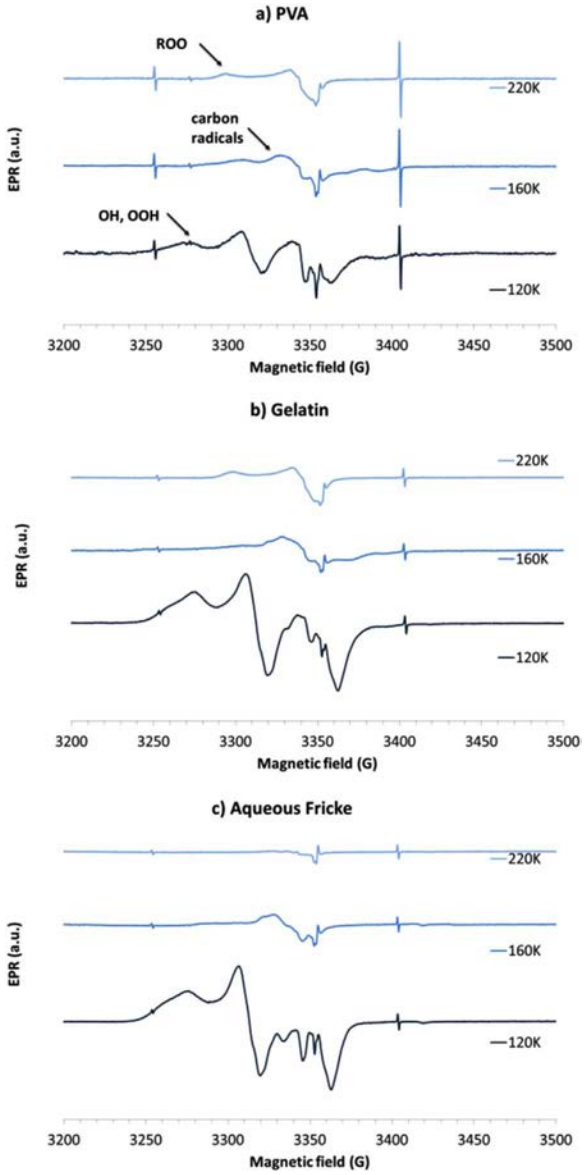

Fig. 1. EPR spectra of Fricke dosimeters made with PVA a), gelatin b) and aqueous solution c) recorded at 120 K after heating at the indicated temperatures.

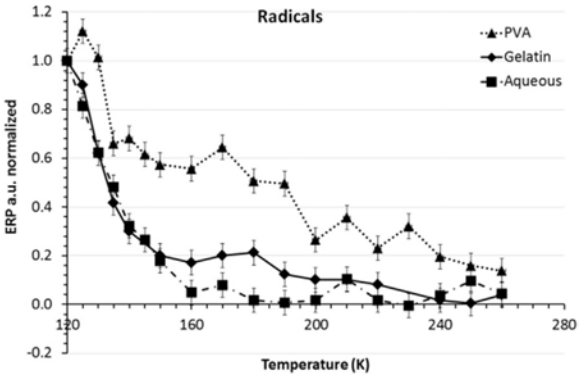

Fig. 2. Variations of radicals concentration with respect the heating temperatures for Fricke dosimeters: (triangles, dashed line) made with PVA, (diamonds, solid line) made with gelatin, (squares, dash-dotted line) in aqueous solution. The data are normalized to the initial EPR signal.

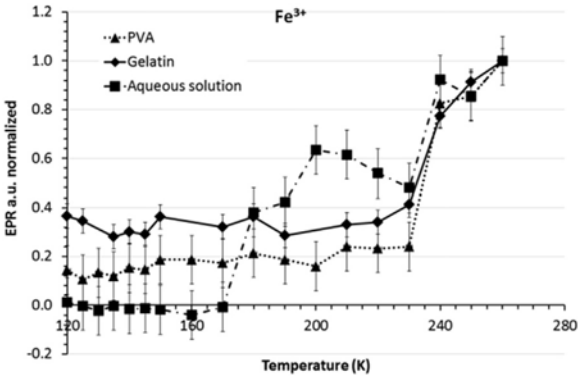

Fig. 3. Variations of radicals concentration with respect the heating temperatures for Fricke dosimeters: (triangles, dashed line) made with PVA, (diamonds, solid line) made with gelatin, (squares, dash-dotted line) in aqueous solution. The data are normalized to the final Fe3+ EPR signal.