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Dose response of Fricke Gel dosimeters with distinct indicators

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Abstract: Fricke solution, composed of ferrous ammonium sulfate in an aqueous solution of sulfuric acid, is used as a chemical dosimeter for gamma rays, X-rays and high energy electrons. The three-dimensional dosimetry has several applications, such as in radiotherapy procedures, imaging diagnosis techniques and internal dosimetry. In this work, the response of Fricke gel dosimeter with two types of indicator was compared. Sodium thiocyanate, a salt not used in dosimetry, and xylenol orange, a well-established indicator, were analyzed as indicators. The studies were performed in a cobalt-60 source. Dosimetric responses of Fricke gel with distinct indicators differ in their sensitivity, that is, the addition of sodium thiocyanate to the gel shifted the saturation point of the gel to an absorbed dose of approximately 300 Gy, while the Fricke gel with xylenol orange presents a saturation of around 30 Gy.

Keywords: dosimetry, Fricke Gel, gamma radiation, indicators.

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Resposta dosimétrica do Fricke Gel com diferentes indicadores

Resumo: A solução Fricke, composta de sulfato ferroso amoniacal em uma solução aquosa de ácido sulfúrico, é utilizada como dosímetro químico para radiaçaõ gama, raios X e elétrons de alta energia. A dosimetria tridimensional possui diversas aplicações, como em procedimentos de radioterapia, técnicas de diagnóstico por imagem e em dosimetria interna. Neste trabalho foi comparada a resposta do dosímetro Fricke gel com dois tipos de indicadores. O tiocianato de sódio, um sal não utilizado em dosimetria, e o alaranjado de xilenol, indicador bem estabelecido, foram analisados como indicadores. Os estudos foram realizados em uma fonte de cobalto-60. As respostas dosimétricas do Fricke gel com indicadores distintos apresentaram uma sensibilidade dosimétrica diferente, isto é, a adição do tiocianato de sódio ao gel deslocou o ponto de saturação do gel para uma dose absorvida de aproximadamente 300 Gy, enquanto o Fricke gel com alaranjado de xilenol apresenta uma saturação em torno de 30 Gy.

Palavras-chave: dosimetria, Fricke Gel, radiação gama, indicadores.

1. INTRODUCTION

Conventional Fricke solution, consisting of ferrous ammonium sulfate in an aqueous solution of sulfuric acid, serves as a chemical dosimeter for gamma rays, X-rays and high energy electrons [1]. This dosimeter is considered a reference standard in radiation chemistry [2]. Oxidation of ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}) is induced when ionizing radiation interacts with Fricke solution. Therefore, Fe^{3+} concentration in Fricke solution depends on the dose absorbed by it [3].

A three-dimensional record of the absorbed dose is possible using gel dosimeters. The conventional Fricke dosimeter has been modified by adding a gelling agent to solution, so it can measure an absorbed dose volumetric distribution [4,5,6,7]. In Fricke gel dosimeter, there is a restriction on Fe^{3+} diffusion due to the gelatin matrix used and after its irradiation, the Fe^{3+} ions produced remain close to its production site. Thus, it is possible to map the delivered dose in gel. Fricke gel can be applied as tissue-equivalent phantoms since its composition is mostly water by weight [1]. Hence, this dosimeter is ideal not only to measure the absorbed dose value in medical treatments like in the Intensity Modulated Radiation Therapy (IMRT), but also absorbed dose spatial distribution in those situations orange [8,9]. Beyond the addition of a gel matrix to Fricke solution, another important modification was the addition of Fe^{3+} indicators, as xylenol orange [10,11]. These indicators increases dosimeter gel stability and, in addition, it makes possible the use of optical analyzes for dosimetric calculations [12].

This study proposes using sodium thiocyanate as indicator for Fricke gel as an alternative to xylenol orange. The present work aims to compare and evaluate the dosimetric response of Fricke Xylenol Gel (FXG) and Fricke gel with sodium thiocyanate when subjected to gamma radiation field.

2. MATERIALS AND METHODS

The gel matrix was prepared with gelatin from porcine skin type A of 300 bloom gel strength (Sigma-Aldrich), at 5 % concentration of final Fricke gel volume. The porcine gelatin was dissolved in tri-distilled water by heating up to 70 °C and shaking in a magnetic stirrer (Fisatom, model 752A), for a period of 10 minutes. After complete dissolution, the sample was cooled at 40 °C for 1 h in an ultrasonic bath. At the same time, the Fricke solution was prepared with 50 mM sulphuric acid (Sigma-Aldrich), 1.0 mM of ferrous ammonium sulphate (Anidrol) and 1.0 mM of sodium chloride (Anidrol), according to ISO/ASTM 51026:2015(E) procedures [2, 13]. After cooling, the porcine gel matrix was mixed to Fricke solution in magnetic stirrer. Two sets of samples were prepared. In one of them was added 0.1 mM of xylenol orange (Synth) and the other 0.3 mM of sodium thiocyanate (Inlab) was added. The final gel was mixed in magnetic stirrer, at room temperature, until the complete indicator dissolution. Fifteen samples were collected of each set and they were stored in polymethylmethacrylate (PMMA) cuvettes, under refrigeration at 2.5 °C in the dark for 24 hours before application.

The Fricke gel irradiation was carried out in a cobalt-60 field, and for that a multipurpose panoramic irradiator installed at the Laboratory of Gamma Irradiation in the Nuclear Technology Development Center (LIG/CDTN) in Belo Horizonte, Brazil, was used. The samples were irradiated with absolute doses ranging from 5 Gy up to 400 Gy. From 5 Gy to 30 Gy the absolute dose was increased in steps of 5 Gy and from 50 Gy to 400 Gy the absolute dose was increased in steps of 50 Gy.

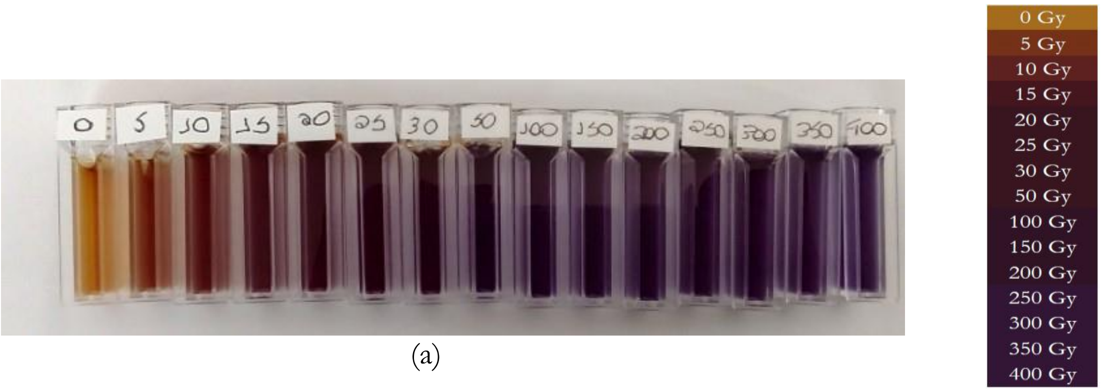
The absorbed dose was measured by using molecular absorption spectroscopy in visible region (spectrophotometer model UV mini 1240, Shimadzu). The wavelength range read varied between 200 nm and 700 nm, since the FXG dosimetric peaks of interest were possibly within this range, according to Baldock and Alves *et al* [10,11]. Fricke gel with sodium thiocyanate is expected to have a change in its hue after irradiation, as is FXG, so reading within this visible wavelength range (200 – 700 nm) will allow dosimetric analysis of the gel.

3. RESULTS AND DISCUSSIONS

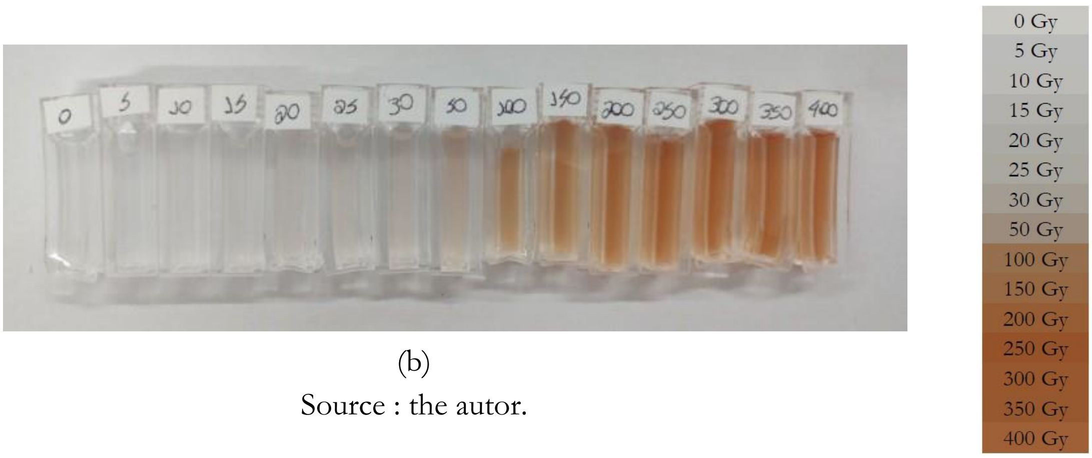
Ferrous ammonium sulphate is the main reagent in Fe^{2+} oxidation as a provider of these ions; the sulphuric acid catalyzes this oxidation and sodium chloride minimizes the effects of organic impurities

In Fig. 1 is shown the results of gamma irradiation of (a) FXG and (b) Fricke gel with sodium thiocyanate. Xylenol orange molecule is able to bind one or two Fe^{3+} ions at their ends, forming chromophores moiety [14,15]. The probability of formation of these complexes depends on Fe^{3+} and xylenol orange concentrations. Since chromophores moiety can change color characteristics of the substance, after the complexation reactions, FXG color changes from orange to violet, which visually highlights the formation of Fe^{3+}.

Figure 1: Color change of samples as a function of absorbed dose ranging from 0 Gy to 400 Gy: (a) Fricke gel with Xylenol orange – FXG and (b) Fricke gel with sodium thiocyanate.



(a)



(b)

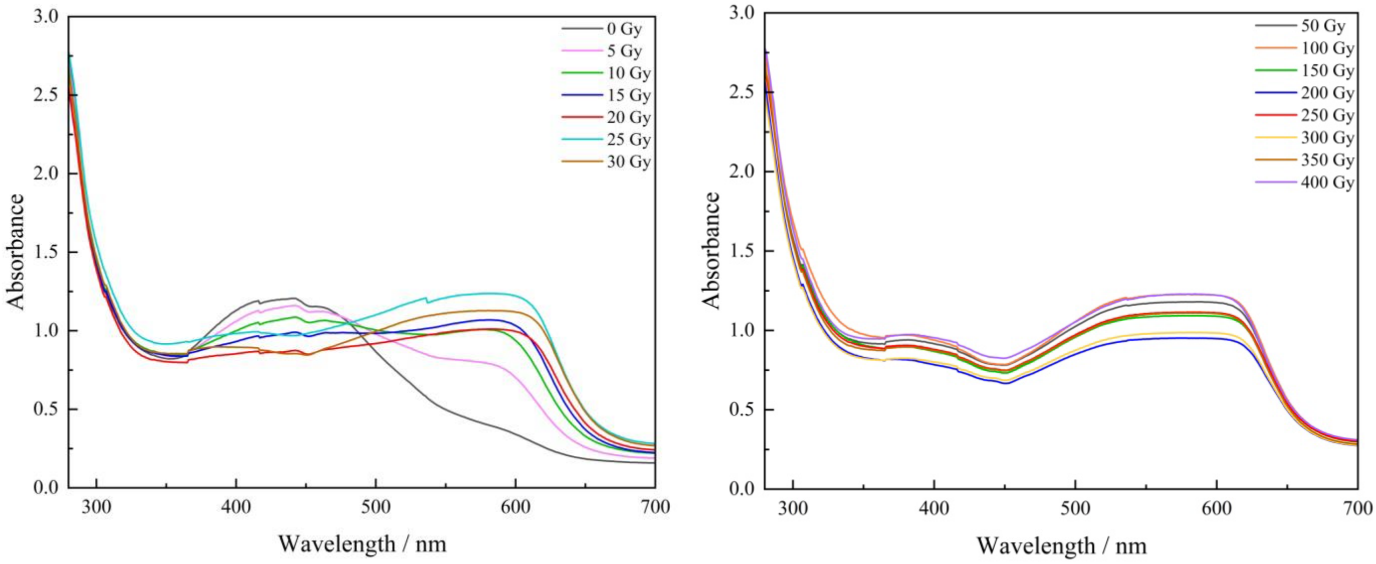
Source : the autor.

Sodium thiocyanate is an ion that also acts as a complexing agent and, therefore, can be used to identify metallic ions, including Fe^{3+} ions. In an aqueous acid medium, the thiocyanate molecule binds with Fe^{3+}, forming the complex hexathiocianoferrate (III), $[Fe(SCN)_6]^{3-}$, whose color is red [15,16,17].

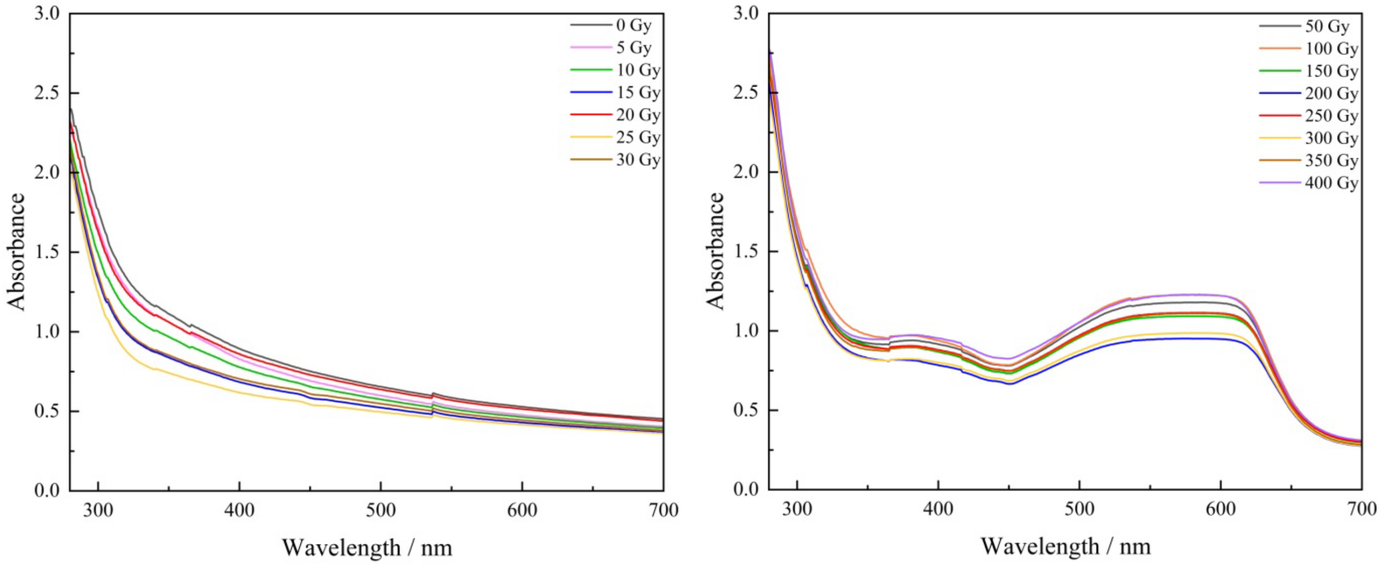
Apparently, FXG presented a possible saturation above an absorbed dose of 20 Gy, since there was no change in tone from this absorbed dose value. On the other hand, Fricke gel with sodium thiocyanate shows color change above an absorbed dose of 15 Gy. The possible saturation on these dosimeter occurred for absorbed doses up to 300 Gy.

The absorption spectra obtained for FXG and Fricke gel with sodium thiocyanate after their irradiations are shown in Fig. 2. The FXG spectrum has two absorption peaks: one at approximately 442 nm, which corresponds to the absorption of Fe^{2+}, and another at 573 nm, corresponding to the absorption of Fe^{3+} produced after irradiation [3]. Hence, as the absorbed dose is increased, the peak located at 442 nm decreases, due to greater oxidation of Fe^{2+}, and an increase in the peak corresponding to Fe^{3+} is observed, since they are produced proportionally to the absorbed dose. In Fricke gel with sodium thiocyanate, a dosimetric peak is observed between 470 nm and 480 nm that corresponds to the absorption of the complex hexathiocyanferrate (III), reddish in tone, produced due to Fricke gel irradiation.

Figure 2: UV-Visible spectrum of absorbed dose ranging from 0 Gy to 400 Gy: (a) Fricke gel with Xylenol orange – FXG and (b) Fricke gel with sodium thiocyanate.



(a)

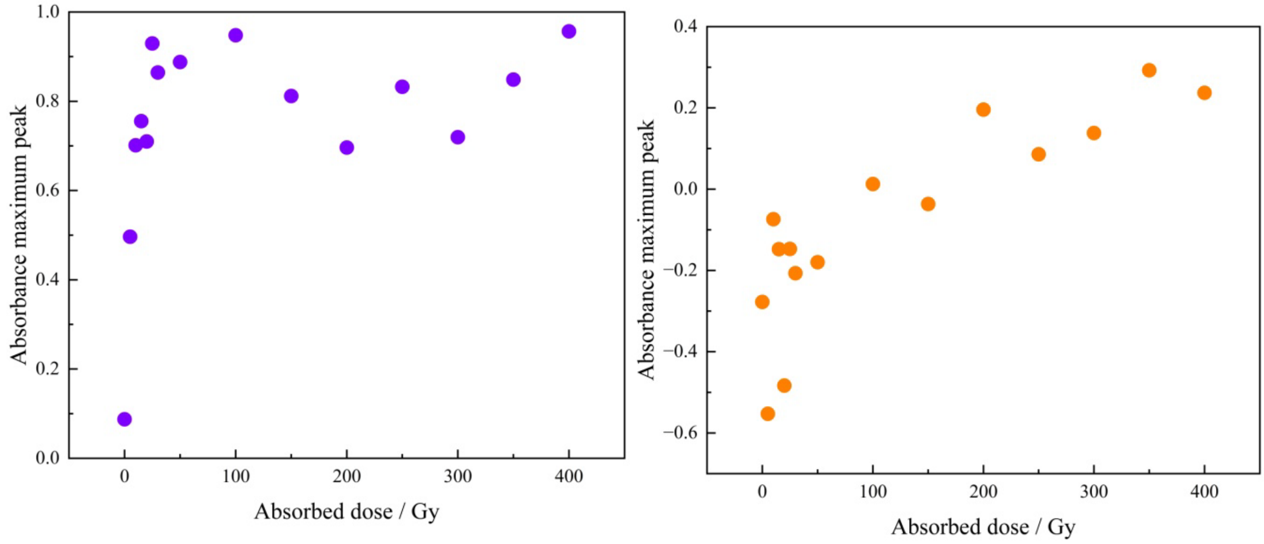


(b)

Source : the autor.

An analysis between absorbance and absorbed dose for FXG and Fricke gel with sodium thiocyanate is shown in Fig.3. It is possible to observe an increase in the maximum absorption peak with increasing in absorbed dose, for small dose values. For higher absorbed dose values, above 50 Gy, FXG was showed saturation. This happens due to complexation reactions between all xylenol orange molecules in gel and Fe^{3+} ions. In Fricke gel with sodium thiocyanate, the maximum absorption peak also increased with an increasing absorbed dose. On the other hand, in that set, the saturation point occurred for a higher absorbed dose compared to FXG set. This increase in saturation point occurred because a single Fe^{3+} ion can bind to several sodium thiocyanate molecules, unlike FXG, whose molecule binds to Fe^{3+} at its ends only [18].

Figure 3: Spectrophotometric dose response as a function of absorbed dose ranging from 0 Gy to 400 Gy: (a) Fricke gel with Xylenol orange – FXG and (b) Fricke gel with sodium thiocyanate.



(a) (b)

Source : the autor.

Different Fricke gel indicators have been proposed in the literature. Alves *et al.* tested the ligands alizarin, bromocresol, green, bromocresol purple, bromothymol blue, calcichrome, citric acid, Congo red, eriochrome black, eriochrome blue, fuchsine, methyl orange, methyl violet, murexide, naphthol green, phenol red and quercetin [11]. Fricke gel doped with methylene blue was analyzed by Souza *et al.* for dosimetry in photodynamic therapy [19]. A formulation of the Fricke gel dosimeter with benzoic acid and methylthymol-blue as indicator was studied by Parwaie *et al.* as a sensitive dosimeter to low dose levels [20]. Several studies analyze sodium thiocyanate as a chelator of ferric ions, but the use of this salt as an indicator for Fricke gel dosimetry shows potential of further investigation.

4. CONCLUSIONS

The new formulation of Fricke gel with sodium thiocyanate demonstrated dosimetric response in the gamma irradiation field. The samples prepared with this indicator exhibited higher sensitivity than those prepared with xylenol orange, a widely used indicator in gel dosimetry. While the FXG presents saturation for doses above 50 Gy, the dosimeter with sodium thiocyanate did not saturate for the absorbed doses provided in this study, which were up to 400 Gy. This alternative Fricke gel formulation present versatile applications in three-dimensional dosimetry, with the potential to modify the upper absorbed dose limit or enhance dosimeter sensitivity by changing chemical components, such as ammonium ferrous sulfate, the gelling agent, or the Fe^{3+} indicator.

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CONFLICT OF INTEREST

All authors declare that they have no conflicts of interest.

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