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Study of the use of sodium thiocyanate as an indicator for three-dimensional dosimetry

Estudo da viabilidade da utilização do tiocianato de sódio como indicador para dosimetria tridimensional

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Abstract

Three-dimensional dosimetry allows the determination of dosimetric quantities with a volumetric gradient. With Fricke Gel it is possible to make measurements of this nature due to the restriction of ions in this dosimeter caused by the presence of a gelatinous matrix. When ion indicators are added to Fricke Gel, the diffusion of the ions is further hampered and, in addition, the use of optical measurement techniques for the determination of the absorbed dose becomes possible. In this study, a new ferric ion indicator possibility for Fricke Gel is evaluated. Sodium thiocyanate was added to the Fricke Gel matrix and the effect of this addition was analyzed in a gamma radiation field and in a high-energy electron beam. The obtained results demonstrated the possibility of using this indicator as a binding agent in the Fricke Gel dosimeter. In the gamma irradiation field, the dosimeter showed a linear response with the absorbed dose between 5 Gy and 150 Gy, in addition to presenting visual evidence of the spatial distribution of the radiation field to which it is subjected.

Keywords: Fricke Gel, three-dimensional dosimetry, optics.

Resumo

A dosimetria tridimensional permite a determinação de grandezas dosimétricas que possuem um gradiente volumétrico. Com o Fricke Gel é possível fazer medições dessa natureza devido à restrição de íons nesse dosímetro ocasionado pela presença de uma matriz gelatinosa. Quando indicadores de íons são adicionados ao Fricke Gel, a difusão dos íons é dificultada ainda mais e, além disso, o uso de técnicas ópticas de medição para a determinação da dose absorvida se torna possível. Nesse estudo, uma nova possibilidade de indicador de íons férricos para o Fricke Gel é avaliada. O tiocianato de sódio foi acrescido à matriz do Fricke Gel e o efeito dessa adição foi analisado em um campo de radiação gama e em um feixe de elétrons de alta energia. Os resultados obtidos demonstraram a possibilidade da utilização desse indicador como agente ligante no dosímetro Fricke Gel. No campo de irradiação gama, o dosímetro apresentou resposta linear com a dose absorvida entre 5 Gy e 150 Gy, além de apresentar evidência visual da distribuição espacial do campo de radiação a que está sujeito.

Palavras-chave*: Fricke Gel, dosimetria tridimensional, óptica.*

1. Introduction

Dosimetry is an important procedure carried out in situations involving the presence of ionizing radiation, as it allows evaluating the dose of radiation absorbed by a volume of matter and, in this way, measuring the effect induced by the incident radiation. Furthermore, the determination of dosimetric quantities, such as the absorbed dose, allows exploring the use of ionizing radiation in different areas, mainly in medicine.

The choice of a suitable dosimeter for carrying out measurements depends on several factors, including the dose range to be measured, type and energy of radiation, effects of influence quantities, cost, availability and safety of this dosimeter, as well as the spatial resolution in the evaluation of radiation fields.

The use of three-dimensional dosimeters, for example, is excellent when there is a gradient of the quantity to be measured. An example is the evaluation of absorbed dose distribution in a patient undergoing a computed tomography examination (1). In the Intensity Modulated Radiation Therapy (IMRT) technique, the use of three-dimensional dosimetry would be ideal not only to measure the dose absorbed in this type of treatment, but also its spatial distribution (2).

An example of a three-dimensional dosimeter is Fricke Gel, proposed by Gore *et al.* in the 1980s (3). This dosimeter is an alternative to conventional Fricke, produced by incorporating the Fricke solution into a gelatinous matrix.

Different gelatinous matrices were proposed to be incorporated into Fricke solution. Animal gelatins, such as porcine gelatin and bovine gelatin, are the most used, and agarose, which has a vegetable source, is also commonly used as a gelling agent for Fricke (4).

Fricke solution is composed of an aqueous solution with ammoniacal ferrous sulfate and sulfuric acid. Proposed in 1927 by Hugo Fricke and Sterne Morse (5), the conventional Fricke is a chemical dosimeter based on the oxidation of ferrous ions (Fe^{2+}) into ferric ions (Fe^{3+}). This process begins with water radiolysis process: when there is absorption of energy provided by ionizing radiation, the hydrogen bonds of the H_2O molecules present in Fricke solution are broken. The species produced in the water radiolysis process will react with the Fe^{2+} ions from the ammoniacal ferrous sulfate, transforming them into Fe^{3+}.

The ferric ions production is related to incident energy on the solution, per unit mass, by equation (1) (4):

$$\Delta\left[Fe^{3+}\right] = \frac{D \cdot G\left(Fe^{3+}\right) \cdot 10\rho}{N_A \cdot e} \quad (1)$$

D is the absorbed dose by Fricke solution, $G(F^{3+})$ is chemical yield of ferric ions, ρ is the Fricke solution density, N_A is Avogadro's number and *e* is electron charge. As described by equation (1), Fe^{3+} concentration depends linearly on energy deposited by incident ionizing radiation on Fricke solution and, therefore, it is possible to infer directly the absorbed dose by determining the production of ferric ions (4).

In Fricke Gel dosimeters, there is a restriction on ions diffusion due to the gelatinous matrix. Therefore, after dosimeter irradiation, the Fe^{3+} ions produced by radiation incidence remains close to their production site, making it possible to detect the volumetric distribution of radiation field. Consequently, Fricke Gel can be used to map the distribution of absorbed dose by the material.

Ion diffusion can also be slowed down by adding Fe^{3+} ion indicators to Fricke Gel. The complex formed between the indicator molecules and the Fe^{3+} ions is heavier than isolated ions; as a result, its diffusion is reduced. This not only increases the stability of the dosimeter, but also improves the spatial definition of dosimetric quantity.

Nowadays, there are some types of indicators that can be used in Fricke dosimetry, such as xylenol orange. Sodium thiocyanate is a salt that can act as a complexing agent and it is widely used to identify metal ions, including Fe^{3+} ions. However, this salt is not used in Fricke Gel dosimetry. In view of this, the objective of this work is to investigate the feasibility of using sodium thiocyanate as an indicator of agarose gelatinized Fricke Gel dosimeter.

Xylenol orange is the most common indicator used in Fricke dosimetry. The molecule of this chelator can bind one or two Fe^{3+} ions at its ends, forming chromophore groups in this molecule (6). These molecule portions formed can absorb light in the visible spectrum. Before the complexes formation, the Fricke solution added with xylenol orange has a yellow or orange color, depending on the concentration of this indicator. After the complexation reactions of Fe^{3+} ions with chelator, the color changes to violet, which visually demonstrates the formation of ferric ions in the dosimeter.

Sodium thiocyanate (NaSCN), in an aqueous acidic medium, binds with Fe^{3+} ions, forming the stable hexathiocyanoferrate (III) complex, $[Fe(SCN)_6]^{3-}$, whose color is red (7). The formation probability of these complexes depends on Fe^{3+} and NaSCN concentration. It is possible to observe changes in the gel color tone with the incidence of radiation, since Fe^{3+} ions quantity depends linearly on absorbed dose by material. This visual change allows the use of optical analyses for dosimetric calculation, relatively simpler measurement techniques.

Agarose is a polysaccharide isolated from seaweed and, when solubilized in water and subsequently gelatinized, it presents high stability and resistance (8). Comparing agarose with to animal gelatins, agarose is more transparent, which facilitates its reading by optical methods.

2. Materials and methods

Fricke Gel gelatin matrix was prepared at a concentration of 1 % (m/v) of the total volume of the dosimeter. For this, agarose (*Uniscience*) was added to tri-distilled water and this mixture was stirred and heated to 150 °C on a magnetic stirrer. After agarose complete dissolution, the mixture was cooled to 50 °C at room temperature so that Fricke solution could be incorporated. The Fricke solution was prepared with the following concentrations: 50 mM sulfuric acid (*Sigma-Aldrich*), 1.0 mM ammonium ferrous sulfate (*Anhydrol*) and 1.0 mM sodium chloride (*Anhydrol*). Sodium thiocyanate (*Inlab*) was added to Fricke solution at a concentration of 0.3 M. The final mixture had a proportion of 75 % (v/v) gelatin matrix and 25 % (v/v) Fricke solution and it was distributed into 15 polymethyl methacrylate cuvettes with 1.5 mL and dimensions of $4.5 \times 10 \times 32\ mm^3$, and into 2 glass containers with 3.4 mL, 7.0 cm in height and 2.5 cm in diameter. The samples were stored under refrigeration at 2.5 °C for 24 hours.

To verify the absorbed dose dependence of gel dosimeter, gamma irradiations were performed in a multipurpose panoramic irradiator containing a cobalt-60 source, installed in the Gamma Irradiation Laboratory (LIG) of the Nuclear Technology Development Center (CDTN). The 15 samples stored in cuvettes were irradiated with an absorbed dose that varied between 5 Gy and 400 Gy. In the range between 5 Gy and 30 Gy, the increment between consecutive doses was 5 Gy, and between 50 Gy and 400 Gy, the increment was 50 Gy.

Absorption spectrophotometry technique, in ultraviolet visible region (UV-VIS) was chosen to perform absorbed dose measurements. For this purpose, a UV mini 1240 spectrophotometer (*Shimadzu*) was used. Measured wavelength range varied between 200 nm and 700 nm, since the dosimetric peaks of interest would possibly be within this range.

In addition, Fricke gel dosimeter produced was exposed to a high-energy collimated electron beam produced in a linear accelerator of the Advanced Radiotherapy Center (*Radiocare* – Oncoclínicas Group) to verify the possibility of using this gel for measurements in three dimensions. The sample stored in the glass containers was subjected to a 2 cm thick field with the equivalent absorbed dose of 30 Gy.

3. Results

3.1. Absorbed dose response

Fricke Gel with sodium thiocyanate added to its matrix presented a significant color change after gamma irradiation. This change, from transparent to a copper tone, was evident at the lowest absorbed dose, 5 Gy, as shown in Figure 1. Above 150 Gy, the dosimeter showed an apparent saturation behavior, since gel color that received absorbed doses above this value became apparently uniform.

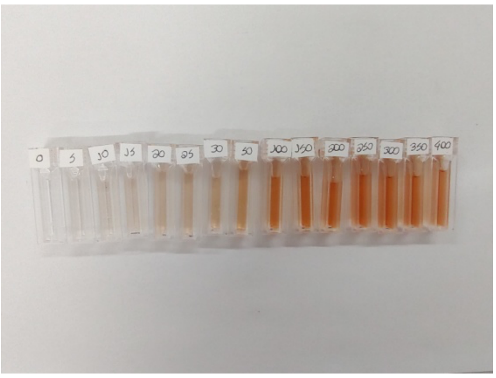

Figure 1. Color change showed by Fricke Gel with sodium thiocyanate indicator after gamma irradiation with absorbed doses ranging from 5 Gy to 400 Gy.

Optical absorption spectra in visible region were obtained for the 15 samples and they are presented in Figure 2.

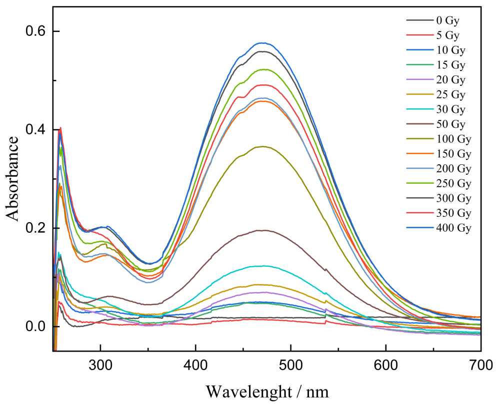

Figure 2. Absorption spectra of Fricke Gel with sodium thiocyanate indicator after gamma irradiation with absorbed doses ranging from 5 Gy to 400 Gy.

Fricke Gel spectra show an absorption peak located at wavelength between 470 nm and 480 nm. It is evident that irradiated dosimeters absorb these electromagnetic wavelength, which correspond to bluish color, and emits wavelengths corresponding to the rest of the visible spectrum, which gives the gels a reddish tone. This peak corresponds to absorption of hexathiocyanoferrate (III) complexes, formed between the chelation between sodium thiocyanate molecules and Fe^{3+} ions produced by gel irradiation.

3.2. Ferric ions spatial restriction

Figure 3 shows the Fricke Gel sample with the sodium thiocyanate indicator irradiated in a high-energy collimated electron beam.

The color change was evident in a portion of the dosimeter volume, whose dimensions were 2.5 cm in height and 2.5 cm in diameter. This measurement was taken 1 hour after the moment of irradiation.

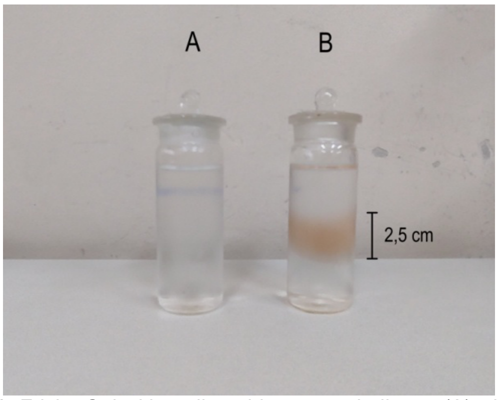

Figure 3. Fricke Gel with sodium thiocyanate indicator (A) without irradiation and (B) after irradiation in a collimated electron beam with an absorbed dose of 30 Gy.

4. Discussion

4.1. Absorbed dose response

Figure 4 shows the spectrophotometric response of Fricke Gel with sodium thiocyanate indicator as a function of absorbed dose. This response was obtained from maximum peak of each absorption spectrum and its respective absorbed dose.

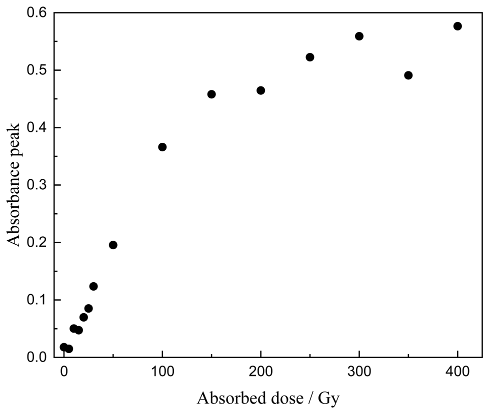

Figure 4. Spectrophotometric response of Fricke Gel with sodium thiocyanate indicator.

Fricke Gel spectrophotometric response increased linearly with the increasing of absorbed dose in range between 5 Gy and 150 Gy. There was saturation for absorbed doses above this value, since the absorbance peak value did not show significant variation.

A linear fit, shown in Figure 5, was made with the points corresponding to absorbed doses belonging to possible useful range of the dosimeter (5 – 150 Gy). This dose-response curve of Fricke Gel has a regression coefficient of around 99 %.

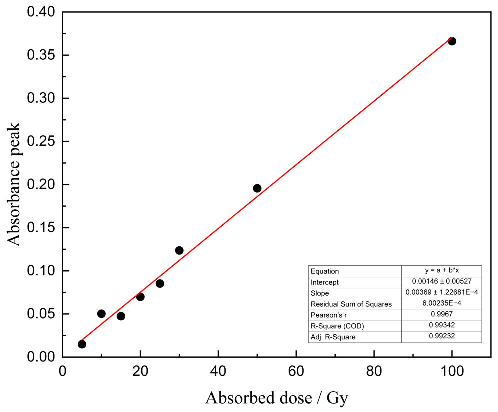

Figure 5. Dose-response curve of Fricke Gel with sodium thiocyanate indicator.

Fricke Gel with xylenol orange indicator, depending on its concentration, presents a saturation for lower absorbed doses in relation to Fricke Gel with sodium thiocyanate. For a xylenol orange concentration of 0.166 mM, for example, the saturation of Fricke gel dosimeter with this indicator occurs for absorbed doses above approximately 30 Gy, as evidenced in the dose-response curve presented in Figure 6 (6).

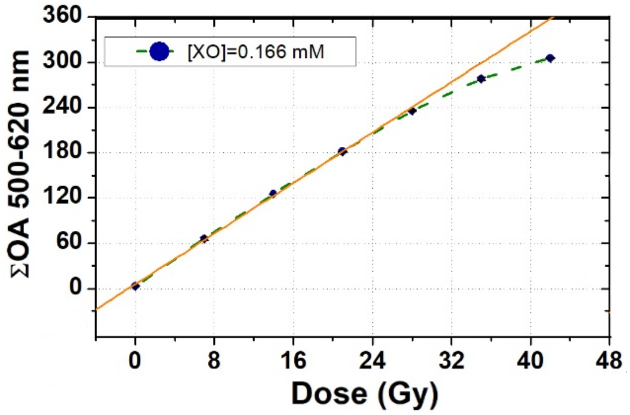

Figure 6. Dose-response curve of Fricke Gel with xylenol orange indicator at a concentration of 0.166 mM[6].

PVA-GTA Fricke gels, dosimeters based on poly-vinyl alcohol (PVA) added to glutaraldehyde (GTA), a small molecule, also presents a saturation for lower absorbed doses in relation to Fricke Gel with sodium thiocyanate. It is possible to observe with PVA-GTA Fricke gels dosimetric response, shown in Figure 7, that the saturation ocurrs approximately above 30 Gy (9).

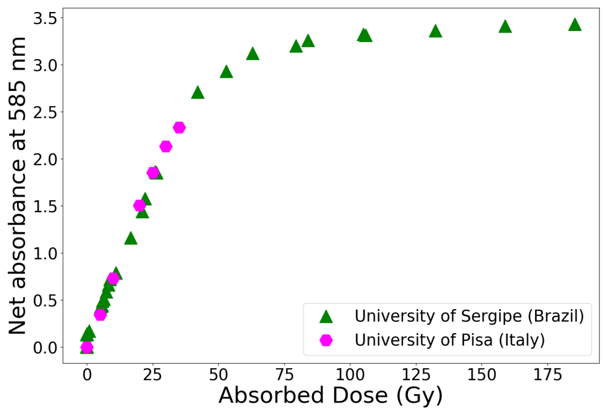

Figure 7. Dose response of PVA- GTA Fricke gels measured with UV-VIS spectrometry at the University of Pisa, Italy, and at the Federal University of Sergipe, Brazil[9].

4.2. Ferric ions spatial restriction

After Fricke Gel with sodium thiocyanate irradiation in a 2 cm thick collimated electron beam in a filament form, it was observed that Fe^{3+} ions formed in irradiation process were restricted to their site of production. The color gradient throughout dosimeter sensitive volume was a qualitative visual evidence of this restriction, since sodium thiocyanate, when complexed with Fe^{3+} ions, forms molecules that have chromophore groups. These groups are responsible for the color attribute in Fricke Gel.

The color contrast of Fricke gel with xylenol orange is not as evident as that provided by sodium thiocyanate indicator. Figure 8 shows the Fricke Gel with xylenol orange positioned inside a head phantom, after its irradiation with X-ray beams with 6 MV, emitted from different angles by a linear accelerator (10). The absorbed dose distribution measurement by dosimeter, in this case, was only possible by computational methods or optical computed tomography (CTO) scanning, more complex measurement methods than optical techniques. Measurement results obtained by a computer program and by a CTO scan are presented in Figure 9 (10).

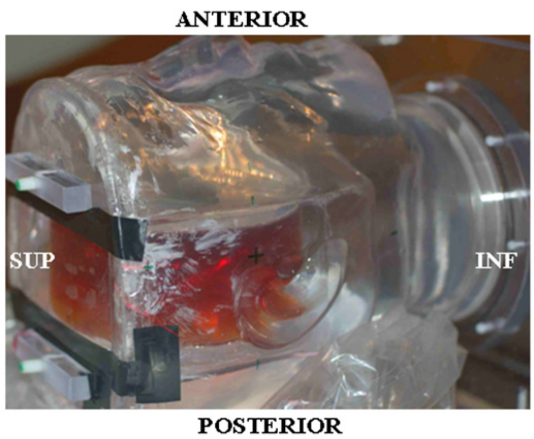

Figure 8. Head phantom filled with Fricke Gel dosimeter with xylenol orange indicator[10].

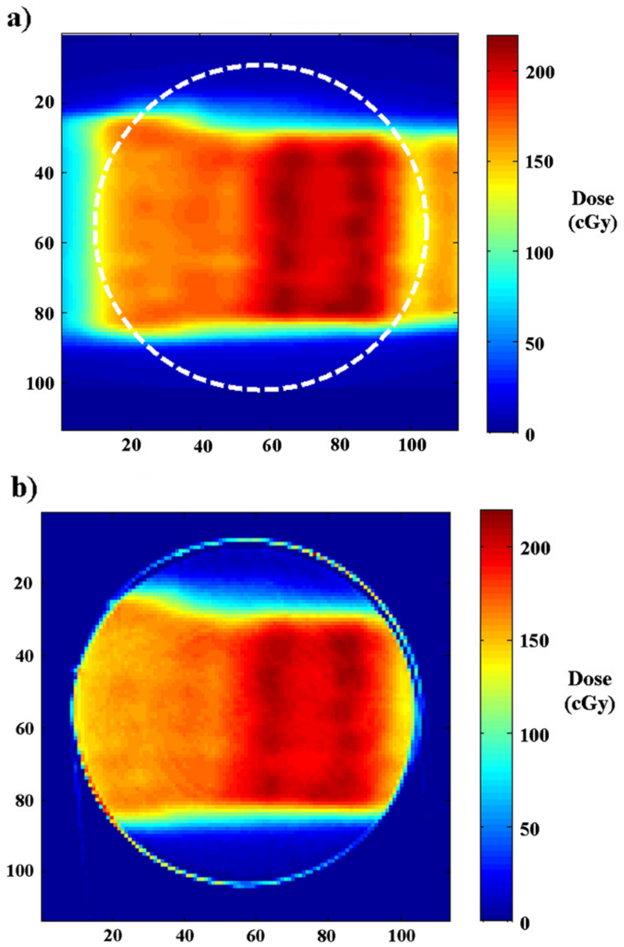

Figure 9. Dose distribution in the coronal plane at a depth of 15 mm in the gel: (a) absorbed dose calculated computationally with Pinnacle software and (b) scanning of the Fricke Gel with computed tomography (VistaTM)[10].

Polymers can also be used as three-dimensional dosimeters. An example is a gel made from a solution of maleimido-pyrene (MPy) in tertiary-butyl acrylate (TBA) (11). This material increases its fluorescence with increasing absorbed dose. The addition of a gelatinous matrix to MPy-TBA solution allows the fluorescence could be fixed in space of its formation. Figure 10 presents a MPy-TBA radio-fluorescence gel with a radioactive seed inside it.

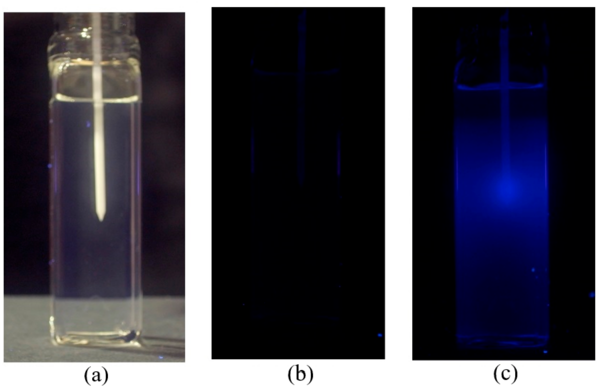

Figure 10. MPy-TBA radio-fluorescence gel with a iridium-192 seed insertion in a catheter (A) under visible-light (B) under UV light prior to seed insertion and (C) under UV light 3 minutes after seed insertion.

5. Conclusions

In this work, sodium thiocyanate salt was added to Fricke Gel dosimeter in order to evaluate the feasibility of its use as an indicator of Fe^{3+} ions. This salt, despite being widely used as a metal ion chelator, is not used for dosimetric measurements.

Primarily, Fricke Gel was prepared using agarose as the gelatinous matrix. The dosimetric studies were performed using a cobalt-60 source, which provided a gamma radiation beam, and a linear accelerator for irradiation with high-energy electrons. The absorbed dose was obtained using the absorption spectrophotometry technique in the UV-VIS region.

According to results, Fricke Gel with sodium thiocyanate indicator presents a dosimetric response both in a gamma irradiation field and in a high-energy electrons field, enabling the use of this indicator for dosimetry.

The dosimeter under study showed a linear response with the absorbed dose after gamma irradiation for range between 5 Gy and 150 Gy. Irradiation in an electron beam demonstrated the restriction of the Fe^{3+} ions produced in dosimeter due to this process, enabling the use of Fricke Gel with sodium thiocyanate for three-dimensional evaluation of absorbed doses.

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