The effect of pH on the characteristics of the methyl red solution as a gamma-ray dosimeter

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Abstract. The effect of the pH on the color change characteristics of the methyl red solution, when exposed by gamma radiation, is the main objective of this study. The color was characterized using a UV-Visible spectrophotometer and a digital photography camera. The used irradiator source is $^{60}$Co with doses varied from 5-100 kGy and a dose rate of 5.5 kGy/h. The color stability was studied by observing the effects of the storage conditions of the solution: temperature, light, and humidity. The original methyl red solution at pH 6.3 has a red color and gives a radiochromic phenomenon with a change of color from red to dark red for a dose of 5-20 kGy, then the color fades and turns colorless gradually at a dose of 25-100 kGy. On the other hand, for a methyl red solution of pH 7.1 before irradiation has a yellow color, turns to dark yellow at doses of 5-25 kGy, then the color fades and becomes colorless at a dose 40 kGy. The color of the methyl red solution at pH 7.1 is more stable against storage light conditions compared to pH 6.3. These results suggest that this methyl red solution can be used as a gamma-ray dosimeter in the dose range of 5-40 kGy.

1. Introduction
Dosimeter plays an important role in quality control of the radiation process [1]. Currently, there are several types of dosimeters used in industrial applications, one of which is a radiochromic dosimeter that utilizes chemical structure changes from indicator dyes when exposed to gamma radiation. Gamma-ray radiation can produce chemical changes in the indicator and if the changes are quantified it can be used as a technique to measure the absorbed dose [2]. Dosimeter film radiochromic have been widely developed as high dose gamma ray dosimeters [3].

In acid-base titrations, organic substances are usually used as indicators. They change color in a certain pH range. Based on the theory of modern quinoids, acid-base indicators have two different chemical structures. The first structure is benzenoid and the other structure is quinonoid, both of which have different colors. The methyl red indicator has a quinonoid (red) structure in the acid medium and a benzenoid (yellow) structure in the base medium [5].

Methyl red is a pH indicator that can be used for radiochromic materials. Ajji has observed methyl red discoloration due to gamma radiation in alkaline solutions and liquid acids. The response in the base medium decreases exponentially with an increase in absorption dose in the range of 50 Gy to 6 kGy, whereas the response of the solution in an acidic state decreases linearly with an increase in absorption dose to 200 Gy [4]. However, the influence of pH associated with the color stability of the methyl red solution for indicators of gamma-ray dosimeters has never been studied.
The purpose of this study was to observe the effect of pH on methyl red solution as a radiochromic indicator. Observations were carried out at a range of gamma rays from 5–100 kGy. Testing the color stability of indicators on the conditions of light, temperature, and humidity during storage before irradiation and stability of the indicator after irradiation has also been carried out.

2. Materials and methods

2.1. Preparation of methyl red solution
Preparation of methyl red solution (Merck) was carried out by dissolving 0.1 g of methyl red powder in 200 ml of 99.9% ethanol solution (JT Baker). This solution is red and has a pH value of 6.3. Some of the solutions are put into a 2 ml plastic ampoule as much as 50 ampules. Then the remaining solution is given 0.5M NaOH until the color of the solution turns yellow, after being measured, the pH of the solution has a value of 7.1. Samples that have a pH of 7.1 are also put into a 2 ml ampoule plastic as much as 50 ampules.

2.2. Irradiation and measurement
The indicator of methyl red solution was irradiated using a Gammacell 220 irradiator with a source of Cobalt-60 at a dose range of 5–100 kGy at a rate of 5.5 kGy / hour. Each experiment involves 3 samples for each radiation dose. The measurement of absorbance of the solution before and after irradiation was carried out using the GENESYS 10S UV-Visible spectrophotometer from Thermo Scientific. Characterization of the absorbance spectrum is carried out at wavelengths between 200-800 nm.

2.3. Testing the stability of the color of the solution to storage conditions
Color stability of the methyl red solution before irradiation was tested for light, temperature, and humidity of the storage conditions. Relative humidity was obtained by conditioning the storage chamber using a salt-saturated solution: MgCl₂ (33%), Mg(NO₃)₂ (53%), NaCl (75%) and KNO₃ (93%) according to the technique designed by Levine et al (1979) [6].

The color stability of the methyl red solution to the storage temperature before irradiation was examined by storing the sample at a temperature of 10⁰C, 25⁰C, 30⁰C, and 40⁰C at 64% relative humidity. And the color stability of the red methyl solution to the storage conditions before irradiation was also investigated by storing the sample in dark and bright conditions at 25⁰C and 64% humidity. Observations on the three stability tests above were carried out for 3 weeks and the data was taken every week. The solution was characterized using a UV-visible spectrophotometer.

3. Result and discussion

3.1. The effect of pH conditioning on the dose response of the methyl red solution indicator
The pH conditioning effect of methyl red solution as gamma-ray dosimeter has been investigated by irradiating the solution at pH 6.3 and pH 7.1 simultaneously using the same source, dose range, and environmental conditions. The effect of pH was observed by comparing the response of the solution dose at both the pH values visually and graphically. In general, changes in the color of the solution can occur due to the administration of absorbent doses that cause changes in the chemical structure of the dye and can also be due to changes in the pH value of the solution. Where the methyl red solution changes to yellow at pH 7.1 [5].

Dose-response from methyl red solution visually can be observed by looking at the color change of solution as shown in Figure 1, where the pH 6.3 changes in the color of the solution from red to dark red in the dose range of 0-20 kGy, then the color of the solution fades gradually from 25-100 kGy. This color change corresponds to the change in the absorbance spectrum obtained using a UV-visible spectrophotometer. while at pH 7.1 the solution changes color from yellow to dark yellow in the dose range of 0-25 kGy then fades and becomes colorless at a dose of 40 kGy. Methyl red is an azo-dye, which has a carboxyl group in ortho position to the phenyl ring of the molecule. Any change in the chemical structure of this molecule (e.g. split of the carboxyl group due to gamma irradiation or
interruption in the conjugated system) could cause a bleaching of the colour of the indicator solution (Ajji, 2006).

The color change result in Figure 1 shows that the solution indicator at pH 7.1 has a better resolution compared to pH 6.3, where the color change can already be seen at a dose of 5 kGy. This indicates that a solution of methyl red pH 7.1 is better used as a radiochromic dosimeter when observed visually.

The absorbance spectrum of the solution indicator has been investigated using a UV-visible spectrophotometer, where a 1:8 dilution is performed first for a methyl red solution versus 99.9% ethanol solvent. Observation of the absorbance spectrum is carried out in the range of 300-650 nm. The absorbance spectrum indicator solution has a peak at a wavelength of 492 nm for pH 6.3 and 404 nm for pH 7.1 for all absorbent doses. The spectrum also shows the fading of color around the peak wavelength as the absorption dose increases to 40 kGy, this is shown in Figure 2. These results are consistent with previous learning [1,4,7].

Relative absorbance of methyl red solution has been measured, where the results are shown in Figure 3. It can be seen that there is a good linearity in the dose range of 0-20 kGy for pH 6.3 solution, while for pH 7.1 linearity shifts in the range of 15-25 kGy. The accuracy of the indicator solution was tested by irradiating 3 solution samples for each absorbent dose and found a precision error <0.90%.

Figure 1. Photograph of color changes of methyl red indicator solutions after irradiated by gamma-ray with a dose range of 0–100 kGy on(a) pH 6.3, and (b) pH 7.1.

Figure 2. Absorption spectra of methyl red solution dosimeter as a function of wavelength for various absorbed doses on(a) pH 6.3, and (b) pH 7.1.
3.2. Stability of methyl red solution to the storage light conditions

The stability of the methyl red solution to the conditions of the storage light was investigated by storing some of the samples in dark conditions, and some in bright conditions. The solution is maintained at 25°C and 64% humidity. Observations were carried out at a wavelength of 492 nm for pH 6.3 solution and at 404 nm for the solution at pH 7.1 every week for 3 weeks of storage. Figure 4a shows that a pH 7.1 solution of methyl red is stable for 3 weeks of storage in both dark and bright conditions. While pH 6.3 solution is more stable when stored in dark conditions than in bright conditions, this is in accordance with previous studies [1]. These results indicate that the pH of the solution affects the stability of the indicator against the storage conditions.

3.3. Stability of methyl red solution after irradiation

Stability of the indicator solution after irradiation has been tested by observing changes in absorbance of the solution stored up to 12 days after irradiation in dark conditions. The solution is maintained at
25 °C and 64% humidity. Observations were carried out at a wavelength of 492 nm for a pH 6.3 solution and at 404 nm for a pH 7.1 solution, at a dose of 10 kGy and 30 kGy every 4 days for 12 days after irradiation.

The results showed that there was no significant change in absorbance up to 12 days of observation both for pH 6.3 and pH 7.1 (see figure 4b). This indicates that the pH of the solution does not affect the post-irradiation stability of the methyl red solution indicator. Stability of the indicator of the post-irradiation solution is in accordance with the results of previous studies [7].

3.4. Effect of storage temperature on methyl red solution before irradiation
The stability of the indicator solution to the conditions of storage temperature before irradiation was examined by storing the samples at a temperature of 10 °C, 25 °C, 30 °C and 40 °C for 3 weeks. The solution is maintained in dark conditions and humidity is 64%. Observations were carried out at a wavelength of 492 nm for a pH 6.3 solution and at 404 nm for a pH 7.1 solution after 3 weeks of storage.

Figure 5a shows that a solution of methyl red pH 6.3 and pH 7.1 is stable for up to 3 weeks of storage at various temperature variations. This indicates that the pH conditioning of the solution does not affect the stability of the indicator against storage temperature conditions.

3.5. Effect of storage humidity on methyl red solution before irradiation
The stability of the methyl red solution to the humidity storage conditions before irradiation was examined by storing the sample at 33%, 53%, 75% and 93% humidity for 3 weeks. The solution is maintained in light conditions and laboratory temperature. Observations were carried out at a wavelength of 492 nm for a pH 6.3 solution and at 404 nm for a pH 7.1 solution after 3 weeks of storage.

Figure 5b shows that there is no significant change in absorbance up to 3 weeks of storage for both pH 6.3 and pH 7.1. This indicates that the pH of the solution does not affect the stability of the indicator of the methyl red solution to moisture storage.

4. Conclusion
Indicator of methyl red solution sensitive to radiation dose and pH value. Where there is a change in the color of the indicator as the radiation dose increases, and the pH value of the solution from red at pH 6.3 becomes yellow at pH 7.1. Indicator of methyl red solution as a radiochromic dosimeter can be
observed qualitatively and quantitatively with each using a characterization tool namely a photographic camera and UV-Visible spectrophotometer. In addition to causing changes in color in the solution indicator, pH conditioning can also affect the radiation dose response and stability of the indicator. Solution at pH 7.1 has a better resolution than in pH 6.3 visually, besides its stability to the storage conditions before irradiation is also superior to pH 6.3. However, the linearity is not good compared to pH 6.3. In addition, both indicators of methyl red solution both at pH 6.3 and pH 7.1 are stable to conditions of temperature and humidity up to 3 weeks of storage, and stable up to 12 days after irradiation.

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References
[1] Kattan M Y, Daher and Alkassiri H 2007 Radiat. Phys. Chem. 76 1195
[2] Akram N G, Bhutto W A and Sharif I N 2016 Int. Scholars J. 3 182
[3] Chen Y-P, Liu S-Y, Yu H-Q, Yin H and Li Q-R 2008 Chemosphere 72 532
[4] Ajji Z 2006 Radiat. Meas. 41 438
[5] Sabnis R W 2008 Handbook of Acid-Base Indicators (United State: Taylor & Francis Group, LLC)
[6] Levine H W, McLaughlin and Miller A 1979 Radiat. Phys. Chem. 14 551
[7] Kattan M and Daher Y 2016 Int. J. Radiat. Res. 24 263