EG0800302

# Crystal Violet and Methylene Green as Low-Dose Liquid Dosimetry Systems

S. Ebraheem[#], W.B. Beshir and H.M. Hassan
*Safety and Dosimetry Department, National Centre for Radiation Research and Technology,*
*AEA, Cairo, Egypt*

## ABSTRACT

**The ultimate aim of the present work is studying of the possibility of using some organic solutions for gamma radiation monitors and to evaluate and characterize the dosimetric properties of these compounds. Crystal violet (CV) and methylene green (MG) aqueous solutions with different concentrations have been prepared and irradiated to different absorbed doses. The solutions were readout using absorption spectrophotometry technique at $\lambda_{max}$ = 592 nm and 614 nm for CV and MG respectively. The maximum useful dose range was investigated and found to be concentration dependent. It was found that the useful dose range was from 10-160 Gy for CV and from 10-200 Gy for MG. The radiation chemical yield, G-value, was calculated for the studied solutions. The pH effect and the effect of different additives, chloral hydrate and ethanol have been also investigated. The pre- and post- irradiation stabilities of these solutions under different storage conditions were studied and the results showed different significant dependence on the storage condition.**

***Key Words: Crystal Violet/ Methylene Green/ Liquid Dosimetry/ Low Dose.***

## INTRODUCTION

A number of novel liquid dosimetry systems constitute significant advances in practical radiation processing, providing more efficient and accurate means of assuring that a given process is meeting specifications. Examples are: Radiochromic solutions – Tetrazolium salts- for broad dose range applications (1-3). Dye solutions, aqueous alcohol or polyvinyl alcohol solutions of methylene blue, methyl orange, or Congo red, which bleach upon irradiation and are measured with a spectrophotometer or densitometer. These may be used for either large – scale liquid – phase dosimetry or for expensive routine processing Dosimetry (4-6). Also, conductimetric systems – liquid solutions or solid matrices, which can be readout by high frequency (oscillometric) or steady – state conductimetry (7)**.** Another dosimetry system is the alanine – triphenyl tetrazolium chloride system (8) which is used for high dose dosimetry and is measured spectrophotmetrically. A. Kovács developed another system of nitro blue tetrazolium containing radiochrimic dye films which were used as dosimeters by measuring absorbed and reflected light (9). S. Ebraheem developed on 2002 a new dyed poly vinyl alcohol film for high-dose applications (10).

The present work deals with measurement of absorption spectra and studying the dye response. In addition, the G- value was calculated and the effect of pH and different additives on the dye response was investigated. The pre- and post- irradiation stabilities were also studied.

---

[#] Corresponding author. Tel.: +20 22747413; fax: +20 22749298.

*E-mail address:* sief_dose@hotmail.com

## EXPERIMENTAL

### Materials

Crystal violet dye (CV), a violet hexamethyl –p- rosaniline chloride dye with the molecular formula $C_{25}H_{30}ClN_3$ and methylene green dye (MG) which is a basic green dye with the molecular formula $C_{16}H_{17}ClN_4O_4S$ aqueous solutions of different concentrations were used.

Crystal Violet

Methylene Green

### Stock Solution

The stock solution of the Crystal violet and methylene green dyes were prepared by dissolving 0. 075 g and 0.0625 g of the dyes respectively in 25 mL of triple distilled $H_2O$ and then the volume was completed to 500 mL in a volumetric flask. The stock concentration obtained was $3.676e^{-4}$ mol/L and $4.12e^{-4}$ mol/L respectively. Different volumes of the stock solution were taken and completed with triple distilled $H_2O$ in a 250 mL volumetric flask to obtain different concentrations of dye solutions (Table 1).

**Table (1): Different concentrations of dosimeter stock solutions applied for radiation induced effect.**

| Crystal Violet Conc. (mol/L) | Methylene Green Conc. (mol/L) |
|---|---|
| $3.68e^{-7}$ | $4.12e^{-6}$ |
| $7.35e^{-7}$ | $8.24e^{-6}$ |
| $1.47e^{-6}$ | $1.65e^{-5}$ |
| $3.68e^{-6}$ | $2.47e^{-5}$ |
| $7.35e^{-6}$ | $4.12e^{-5}$ |
| $1.10e^{-5}$ | $6.18e^{-5}$ |
| $1.47e^{-5}$ | $8.24e^{-5}$ |
| $2.57e^{-5}$ | |
| $3.68e^{-5}$ | |

### Irradiation Method

The irradiation of the dosimeter solution tubes has been carried out at the central position of the sample chamber using a specially designed wooden holder which maintains the center of the sample chamber at a position of 10.5 cm from the bottom of the sample chamber. This place is the most uniform isodose in the chamber, and it is accurately calibrated.

The tubes were numbered, measured spectrophotometrically. After that, the samples were subjected for irradiation to various doses through removing sequentially 3 tubes at each dose, one after another until the highest dose is reached. The irradiated solutions were then readout spectrophotometrically at characteristic $\lambda_{max}$. The absorption spectra of the unirradiated and irradiated dosimeter solutions were measured through the wavelength range 200-800 nm using a UVIKON 860 spectrophotometer (product of KONTRON Co. Ltd., Switzerland). These solutions were placed into a quartz cell of 1 cm path length designed specially for reproducible fitting into the sample beam of the instrument. The absorbance spectra were scanned to determine the wavelengths (nm) of the maximum absorbance ($\lambda_{max}$) and the change in absorbance for UV/VIS spectra were recorded. The spectral UV/VIS measurements were undertaken at selected $\lambda_{max}$ wavelength (nm) for each tested solutions before and after irradiation. For establishment of the response functions, different calculation techniques were used, e.g. calculating the change in $(\Delta A{\cdot}mm^{-1})_{□}$, or $(\Delta A/A_o)_{□}$, where $\Delta A = | A_o - A_i |$ and $A_o$ and $A_i$ are the absorbance before and after irradiation, respectively. The average response value of each three tubes corresponding to an absorbed dose was plotted against absorbed dose (in Gy) producing response curves.

## Irradiation Sources

The Gamma cell 220 Excel, a $^{60}$Co irradiation facility (manufactured by MDS Nordion, Canada), with activity of 11994.8 Ci at the time of installation (18 Jan. 2002) and absorbed dose rate found to be in the range 7.845-7.666 kGy.h$^{-}$1 overall the time of the work. The overall uncertainty of the absorbed – dose rate is ±2.4 % at the 95 % confidence level.

## Synergetic Effects

The effect of pH was investigated in order to study its effect on the dosimeter response and dye degradation. The pH of the dye solutions was adjusted to different pH values (2, 4, 6, 8, 10, 12) using Hanna Instrument HI Microprocessor pH meter knowing that the actual pH of the dye solutions is 7. The absorbance for different solutions was measured at $\lambda_{max}$ before and after irradiation of the solutions. $\Delta A/A_0$ % was plotted against pH value.

The effect of different additives with different concentrations, as ethanol, nitric acid and chloral hydrate, on dye solution response at constant dye concentration was investigated. The absorbance for different solutions was measured at $\lambda_{max}$ before and after irradiation of the solutions. $\Delta A/A_0$ % was plotted against additive concentration.

# RESULTS AND DISCUSSION

## Absorption Spectra

For different CV and MG concentrations the absorption spectra were recorded before and after irradiation to different doses. Figure 1, 2 shows the results of aqueous solution of CV and Mg of concentrations 1.47 x $10^{-5}$ mol/L and 8.24 x $10^{-5}$ mol/L respectively. The absorption band of the unirradiated solution is noticed in the visible region peaking at 592 nm and 614 nm wavelengths characteristic to violet color and blue color respectively. Upon irradiation, the amplitude of these peaks decrease gradually with the increase of absorbed dose. This radiation induced decrease in absorption band can be said to be due to radiation induced degradation of the main skeleton of the dye molecule.

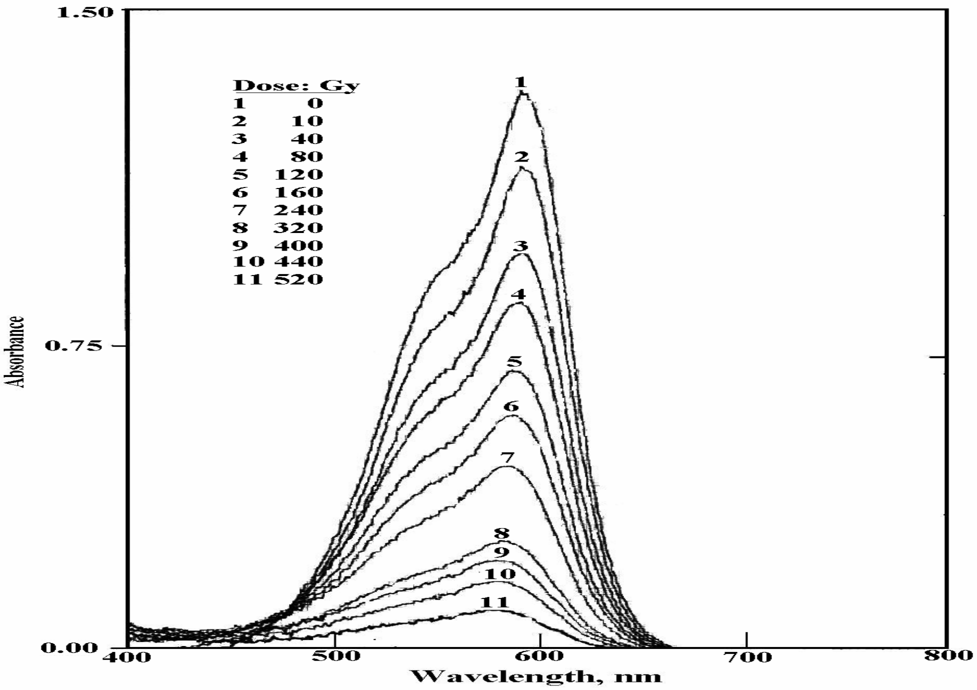


**Fig. 1:** The absorption spectra of CV aqueous solutions unirradiated and irradiated to different doses, [CV] = 1.47 × $10^{-5}$ mol/L.

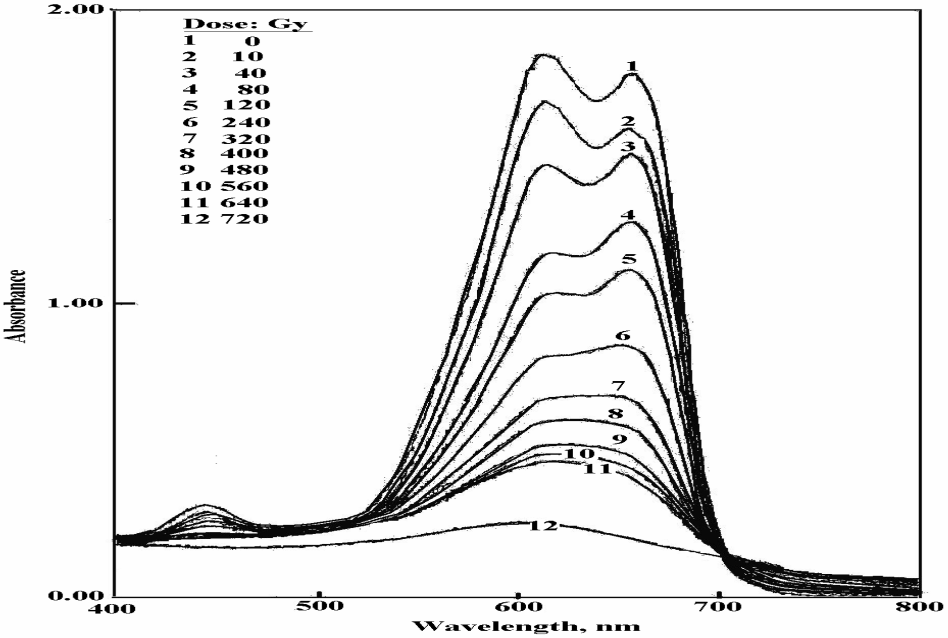


**Fig. 2:** The absorption spectra of MG aqueous solutions unirradiated and irradiated to different doses, [MG] = 8.24 x $10^{-5}$ mol/L

## Response Curves

The response curves of the solutions of CV and MG dyes at different concentrations measured by absorption spectrophotometry in terms of change in absorbance ($\Delta A.\ mm^{-1}$) at $\lambda_{max}$ =592, 614 nm respectively versus the absorbed dose is shown in figures 3 and 4. [$\Delta A = A_0 - A_i$ where $A_0$ and $A_i$ are the relative absorbencies of the unirradiated and irradiated solutions respectively).

From the figure, it can be noticed that for CV the useful dose range is ranging from 10 – 160 Gy, in the concentration range $3.676 \times 10^{-7}$ to $7.35 \times 10^{-6}$ mol/L. In higher concentrations the useful dose range extends up to 500 Gy in the concentration range $1.1 \times 10^{-5}$ to $3.676 \times 10^{-5}$ mol/L. On the other hand for MG it the useful dose range is ranging from 10 – 200 Gy, in the concentration range $4.12 \times 10^{-6}$ to $2.47 \times 10^{-5}$ mol/L. In higher concentrations the useful dose range extends up to 500 Gy in the concentration range $4.12 \times 10^{-5}$ to $8.24 \times 10^{-5}$ mol/L.

Figure 5 is showing the response (slope of the straight parts in the curves given in figure 3,4) as a function of CV, and MG dye concentration. It can be deduced that for CV the response increase sharply up to concentration $1.47 \times 10^{-5}$ then the increase rate begins to slow down at higher concentrations. As for MG the response increase sharply up to concentration $1.1 \times 10^{-5}$ then the increase rate begins to slow down at higher concentrations. This may be due to the cluster formation of the dye at high concentrations.

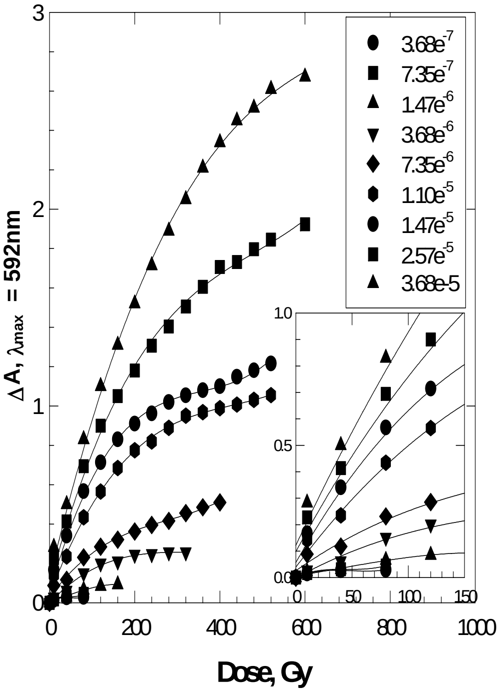


**Fig. 3: Change of response of CV dye solution (ΔA) as a function of absorbed dose, $\lambda_{max}$ = 592 nm**

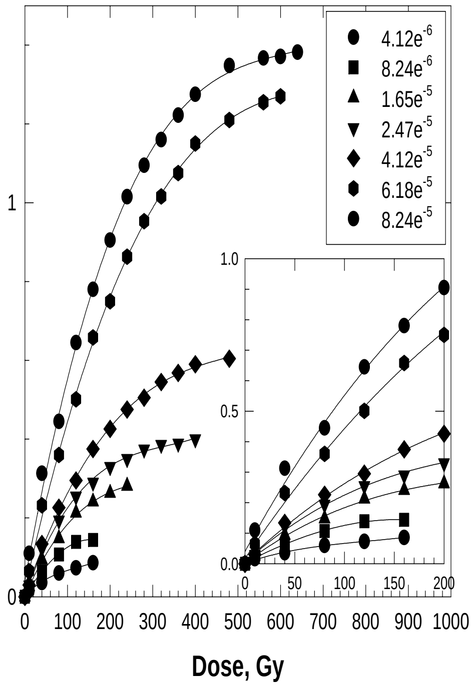


**Fig. 4: Change of response of MG dye solution (ΔA) as a function of absorbed dose, $\lambda_{max}$ = 614 nm**

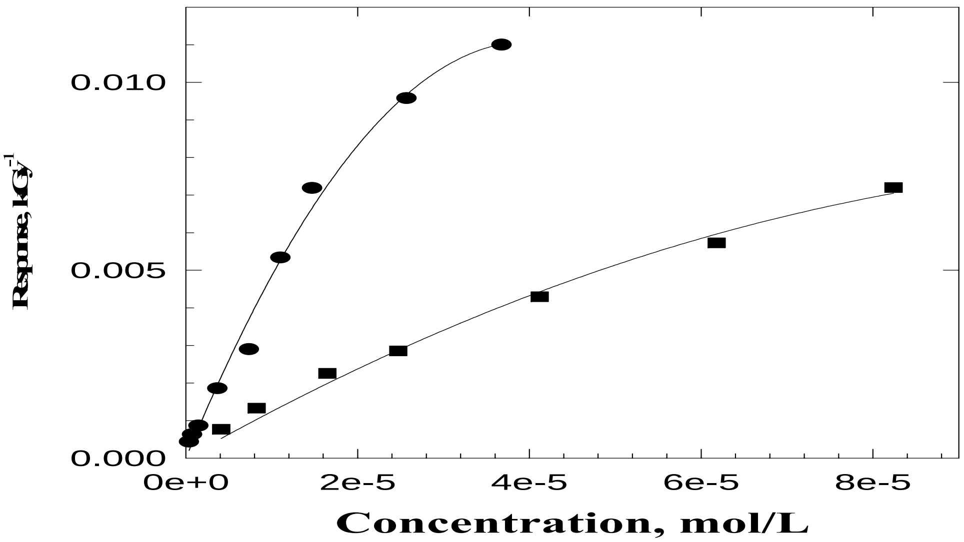


**Fig. 5: Change of the response (slope of straight parts in the curves given in fig. 3,4) as a function of CV and MG dye concentrations**

## The Radiation Chemical Yield (G-Value)

The radiation chemical yield G-value is calculated for CV and MG dyes from the general relation: (18)

$$G(\text{dye}) = \quad \Delta A/D.\varepsilon.\rho.b \qquad\qquad (\text{mol/J})$$

Where, $\Delta A$ is the change in absorbance at $\lambda_{max}$, b is the optical path length (cm), $\varepsilon$ is the linear molar extinction coefficient at $\lambda_{max}$ (L.mol$^{-1}$cm$^{-1}$), $\rho$ is the density of the dosimeter (g.cm$^{-3}$), D is the absorbed dose (Gy).

Using the dye concentration in mol/L and the average value of $A_0/b$, the molar extinction coefficient is calculated as 88272.9 L.mol$^{-1}$cm$^{-1}$ and 21174.7-L.mol$^{-1}$cm$^{-1}$ for CV and Mg solutions respectively. Using the density of water (g.cm$^{-3}$) is to calculate the G-value in terms of µmol/J. The calculated G- value was shown in figure 6a, b at different doses as a function of initial dye concentration. G-value was found to increase in a semi linear mode over the whole dose range and the linearity seams to appear clearly at higher doses. These results encourage the use of such due for dosimetric purposes because of its sequential degradation reaction with gamma ray.

## The effect of pH on the dye response

The degradation behavior at different pH values (from 2 to 12) at a dose of 300 Gy and dye concentration [CV] = 1.72 x 10$^{-5}$ ml/L and [MG] = 3.621 x 10$^{-5}$ ml/L have been studied. Figure 7 shows the degradation behavior versus pH. Measuring the actual pH of the dye solution it was found to be around pH 7 for both dyes. On variation of the pH over the whole range from 2-12, it can be seen that for CV up to pH 8 the degradation behavior is around the value obtained for pH 7 although it decreases with approximately 8 % at pH 2. At pH values above 8, the degradation percentage increases sharply to reach about 180 % at pH 12. The explanation of the observed behavior versus pH must be connected with the free Cl$^-$ radical present in the compound structure. In fact, the degradation scheme depends on the relative reactivity of the compound and the structure of the dye molecule. As for MG it can be seen that at pH 2 the increase in H atom concentration decrease the rate of dye degradation. At pH 12 the OH$^\bullet$ dissociates to O$^-$ and H$^+$. The reactivity of O$^-$ is much lower and so decreases the rate of dye degradation. Therefore we can say that the presence of OH$^\bullet$ increase the dye response to radiation which is around pH 7.

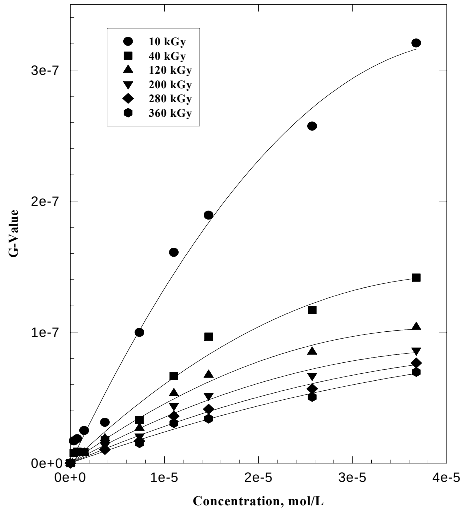


**Fig. 6a: Change of G-value at different doses as a function of CV dye concentration**

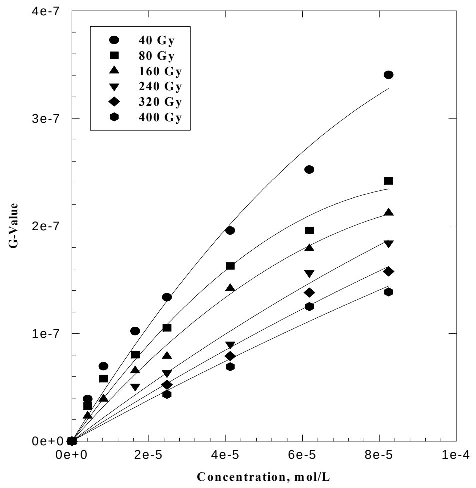


**Fig. 6b: Change of G-value at different doses as a function of MG dye concentration**

### ***The effect of chloral hydrate on the dye response***

The absorption spectra of dye solutions of concentration [CV] =2.9x 10$^{-6}$ mol/L and [MG] = 1.086 x 10$^{-5}$ mol/L containing different concentrations of chloral hydrate irradiated to dose of 300 Gy were studied.

Figure 8 shows the degradation behavior versus chloral hydrate concentration. Normalizing the degradation percentage one can see that for CV the addition of chloral hydrate with whatever concentration leads to an increase in the degradation percentage and this increase is sharp with the least amount of chloral hydrate to reach 2.5 folds of the normal and tends to stabilize on increasing chloral hydrate concentration. This means that the presence of Cl$^-$, resulting from the degradation of irradiated chloral hydrate, encourage the degradation of the dye skeleton. On the other hand for MG the addition of chloral hydrate leads to an increase in the degradation percentage. This increase is unnoticed at small chloral hydrate concentration then increases dramatically with the addition of more chloral hydrate to reach 5 times of the normal rate at certain high value, and then tends to stabilize on increasing chloral hydrate concentration

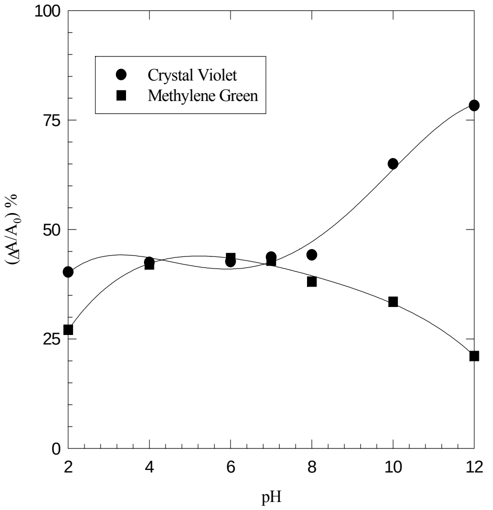
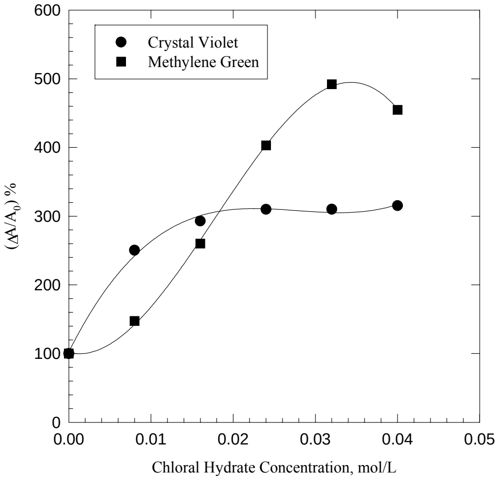


**Fig. 7: Normalization percentage ($\Delta A/A_o$) versus pH, [CV] = 1.72 x $10^{-5}$ and [MG] = 3.62 x $10^{-5}$ at dose 300 Gy**

**Fig. 8: Normalization percentage ($\Delta A/A_o$) versus chloral hydrate concentrations, [CV] = 2.9 x $10^{-6}$ and [MG] = 1.09 x $10^{-6}$, dose 300 Gy**



## The effect of ethanol on the dye response

The absorption spectra of dye solutions of concentration [CV] = 1.57 x $10^{-5}$ mol/L and [Mg] = 1.45 x $10^{-5}$ mol/L containing different concentrations of ethanol irradiated to dose of 300 Gy were studied.

Figure 9 shows the degradation behavior versus ethanol concentration. Normalizing the degradation percentage, one can notice that for CV the addition of ethanol leads to an increase in the degradation percentage. It can be seen that the effect of addition of ethanol is noticed until certain volume addition which may be considered as transition point. Beyond this point any further addition of ethanol leads to the same extent of increase. So in order to study the effect of ethanol as additive it is studied at small volumes of ethanol before this transition point. As for MG the first addition of ethanol with the least quantity leads to a decrease in the degradation percentage. We may say that although ethanol is a good scavenger for the OH radical of the aqueous solution that is responsible for the dye degradation, the presence of a free Cl radical inverses this effect dramatically in case of CV and leads to sharp degradation percentage increase to reach 16 folds of the normal at maximum ethanol concentration**.** As for MG an increase in the dye degradation is noticed which reach 1.3 folds at maximum ethanol concentration.

## The effect of nitric acid on the dye response

The absorption spectra of dye solutions of concentration [CV] = 1.37 x $10^{-5}$ mol/L and [MG] = 1.54 x $10^{-5}$ mol/L containing different concentrations of nitric acid irradiated to dose of 300 Gy were studied.

Figure 10 shows the degradation behavior versus nitric acid concentration. Normalizing the degradation percentage, one can see that in the case of CV the addition of nitric acid leads to an increase in the degradation percentage. It can be said that although the addition of nitric acid leads to a decrease in pH to pH = 2 which should decrease the degradation percentage as mentioned in the pH effect, but it was found that an increase occur in the degradation percentage. This increase may be attributed to the presence of the acidic proton, which reacts with the nitrogen lone pair of electron present in the main dye molecule. On the other hand for MG also the addition of nitric acid leads to a slight increase in the degradation percentage. This increase continues until certain nitric acid volume to reach 130 %. After that the degradation percentage drops to reach 94 % of its original value. The decrease may be attributed to the drop in pH to 2 which agrees with the pH study. So we can say that nitric acid addition leads to a limited increase in degradation percentage. Up to certain value of pH the effect is reversed to inhibit the degradation of the dye at higher concentrations of nitric acid (pH goes close to 2)

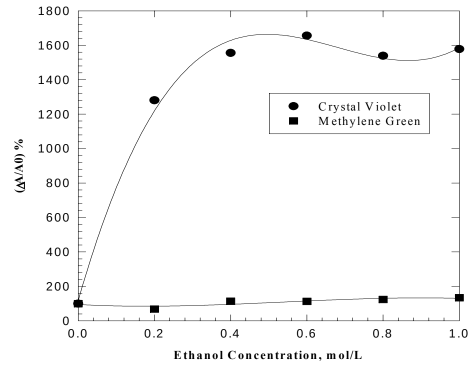


**Fig. 9: Normalization response percentage ($\Delta A/A_o$%) versus ethanol concentration, [CV] = 1.57 x 10-5 mol/L, [MG] = 1.45 x 10-5mol/L, dose = 300 Gy**

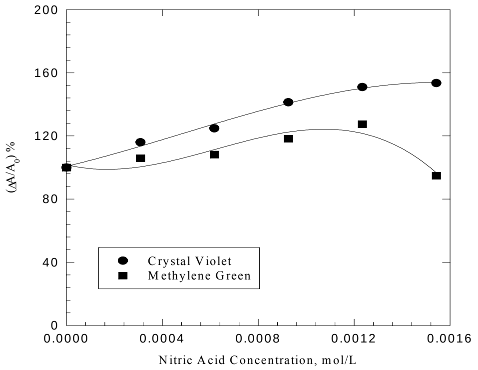
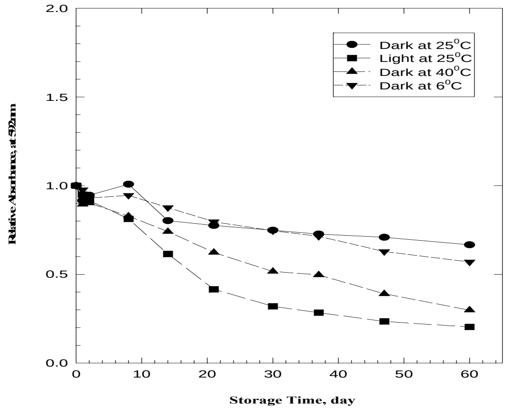


**Fig. 10: Normalization response percentage ($\Delta A/A_o$%) versus nitric acid concentration, [CV] = 1.37 x 10-5 mol/L, [MG]= 1.54 x 10-5mol/L-5mol/L, dose = 300**

## Pre- irradiation stability

Figure 11a, b show the stability of dye solution [CV] = 1.72 x $10^{-5}$ mol/L and [MG] = 3.62 x $10^{-5}$ mol/L stored in dark at different temperatures (namely 6, 25, $60^oC$) and indirect light at 25 $^oC$ before irradiation. The solutions were measured at different intervals during the two months of storage by using UV-spectrophotometry at 592 nm and 614 nm wavelengths respectively. The CV solution stored in dark at 25 $^oC$ also decreases reasonably after 8 days to within 10 % while MG show reasonable stability for about 8 days after preparation where the absorbance decreases within -5 %. . The unirradiated CV solutions stored at 6 $^oC$ in dark show reasonable stability for about 8 days after preparation where the absorbance changes within - 6 %while those stored in 60 $^oC$ in dark and 25 $^oC$ in light decreases sharply within 8 days by 25 % of their original value. As for MG the solutions stored in dark at 6 and 60 $^oC$ and in light at $25^oC$ decrease sharply after 8 days to within 35, 45 and 60 % of their original values respectively.

After that, the absorbance of CV shows a gradual decrease to reach about 60% of its initial value at the end of two months storage period for those stored at dark at 6 and 25 $^oC$. The solutions stored in dark at 60 $^oC$ and 25 $^oC$ in light shows a sharp decrease in absorbance to reach about 20 % of its initial value after the storage. On the other hand for MG the absorbance decreases to reach around 20-40 % of its initial value at the end of two months storage period. Therefore the best storage condition for the stock solution is in dark at 25 $^oC$.



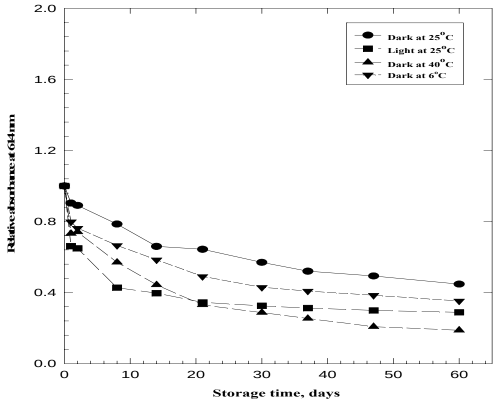


**Fig. 11a: Pre-irradiation stability of CV dye solution stored in dark at different temperatures and light at $25^oC$ [CV] = 1.72 x $10^{-5}$ mol/L**

**Fig. 11b: Pre-irradiation stability of MG dye solution stored at dark at different temperatures and light at $25^oC$, [MG] = 3.62 x $10^{-5}$ mol/L**

## *Post irradiation stability*

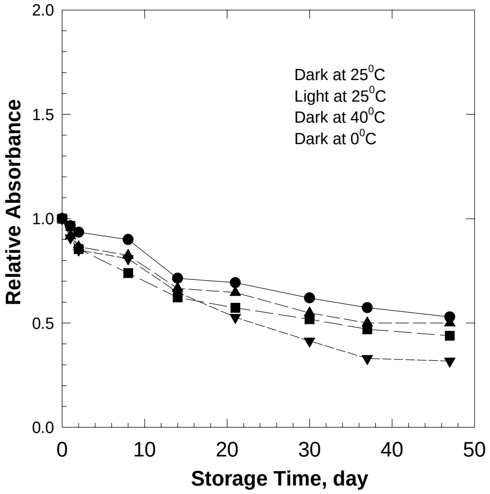
Figure 12a, b shows the stability of irradiated dye solution, [CV] = 1.72 x $10^{-5}$ mol/L and MG] = 3.62 x $10^{-5}$ mol/L at dose 300 Gy stored in dark at different temperatures (namely 6, 25, $60^oC$) and indirect light at 25 $^oC$. The solutions were measured at different intervals during the two months of storage by using UV-spectrophotometry at 592 nm and 614 nm wavelengths respectively. From the figure, it can be concluded that the stability of irradiated CV solutions followed spectrophotmetrically at 592 nm is much better for solutions stored in dark at 6 and 25

$^{o}$C which was found to decrease about 6 % in a period of 8 days. Through the rest of the storage period it decreases to reach about 70 % of its original value. For solutions stored in dark at 60 $^{o}$C and in light at 25 $^{o}$C the absorbance decreases 20 % of its original value in the first 8 days then continue to decrease to reach 35 % of value by the end of storage period. As for MG the stability of irradiated solutions is much better for solutions stored in dark at 6 which was found to decrease about 10 % in a period of 8 days. Through the rest of the storage period it decreases to reach about 50 % of its original value. For solutions stored in dark at 25 $^{o}$C and in light at $^{o}$C the absorbance, decreases 18 % of its original value in the first 8 days then continues to decrease to reach around 40 % of value by the end of storage period. For the solution stored at dark at 60 $^{o}$C the absorbance decrease by 25 % in the first 8 days then decrease to reach 40 % of its original value at the end of the two months.

## CONCLUSION

It was found that CV and MG have absorption bands at 590 nm and 614 nm respectively, which decrease in its intensity with the increase in the irradiation dose. A response curve was drawn at different concentrations to reveal that the useful dose range varies from 10 – 160 Gy for CV and 10 – 200 Gy for MG depending on dye concentration.

The radiation chemical yield was calculated and found to increase, almost linearly, all over the whole dose range for both dyes. The effect of pH on dye response was studied and one can see that the response is not affected in the pH range 2-8 while the degradation is accelerated 2 folds at pH 12 for CV while for MG it was found that the acidic and basic pH values (2, 12) enhance the dye degradation and consequently decrease the dye response sensitivity. Additives effect was studied and generally it was found that all additives accelerate the degradation in case of CV i.e. increase the response sensitivity. As for MG it was found that chloral hydrate and ethanol accelerate the sensitivity while nitric acid increases the sensitivity up to certain volume of acid till the increase in acid volume leads to a drop in pH to the acidic value, the sensitivity decrease once more to lower than normal values The pre- and post irradiation stability studies revealed that the best storage conditions for CV solutions is dark at 6°Cand 25°C while it is for unirradiated solutions is in dark at 25°C while for the irradiated solutions in dark at 6°C for MG.



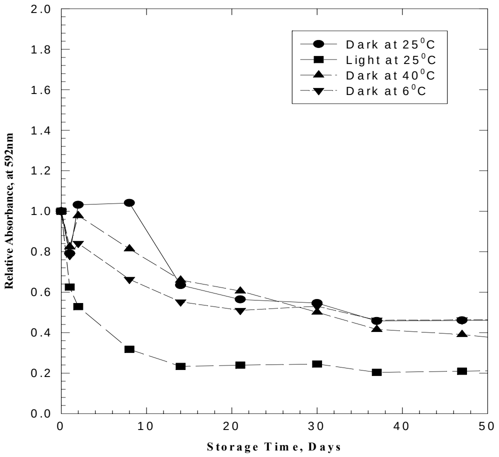


**Fig. 12a: Post-irradiation stability of CV dye solution stored in dark at different temperatures and light at 25°C [CV] =1.72 x $10^{-5}$ mol/L, dose=300**

**Fig. 12b: Post-irradiation stability of MG dye solution stored in dark at different temperatures and light at 25°C [MG] =3.62 x $10^{-5}$ mol/L, dose=300**

## References:

1. A. Kovács, L. Wojnárovits, W.L. McLaughlin, S.E. Ebrahim Eid and A. Miller. Radiat. Phys. Chem.**47,** 483-486 (1996).
2. M. AL-Sheikhly, W.L. McLaughlin, A. Christou and A. Kovács. IAEA-SM-**356/62**.
3. A. K. Pikaev and Z.K. Kriminskaya. Radiat. Phys. Chem.**52,** 555-561 (1998).
4. A. Kovács, L. Wojnárovits, C. Kurucz, M. AL-Sheikhly and W.L. McLaughlin. Radiat. Phys. Chem. **52,** 539-542 (1998).
5. W. H. Chung and A. Miller. Nucl. Technol. **106**, 261-264 (1994).
6. H. M. Khan and M. Anwer. IAEA-SM-**356/22**.
7. I. Slezásk, A. Kovács, W.L. McLaughlin and S. D. Miller. IAEA-SM-**356/28**
8. S. Ebraheem, W. B. Beshir, A. Kovas, L. Wojnarovits, W. L. Mclaughlin. Radiat. Phys. Chem. **55,** 785-787 (1999).
9. A. Kovacs, M. Baranyai, L. Wojnarovits, I. Slezsak, W. L. Mclaughlin, A. Miller, A. Moussa. Radiat. Phys. Chem. **57,** 711-716 (2000).
10. S. Ebraheem, S. Eid, A. Kovacs. Radiat. Phys. Chem. **63,** 807-811 (2002).
11. W.L. McLaughlin, A. W. Boyd, K. H. Chadwick, J. C. McDonald and A. Miller. Dosimetry for Radiation Processing, Taylor and Francis, London (1989).