# Gamma Dosimetry Using Some Dyes in Organic Solvents Solutions at 295 and 77 K

A L Melendez-Lopez[1,3], A Paredes-Arriaga[1], J Cruz-Castaneda[1,3], A Negron-Mendoza[1*], S Ramos-Bernal[1], M Colin-Garcia[2] and A Heredia[1]

[1]*Institute of Nuclear Sciences, National Autonomous University of Mexico (UNAM), PO Box 70-543, 04510 Mexico City, Mexico*

[2]*Institute of Geology, National Autonomous University of Mexico (UNAM)*

[3]*Master's and PhD Program in Chemical Sciences, National Autonomous University of Mexico (UNAM), PO Box 70-543, 04510 Mexico City, Mexico*

*Email: negron@nucleares.unam.mx

## ARTICLE INFORMATION

## ABSTRACT

The aim of this work is to study the behavior under irradiation of different dyes (green malachite, methyl orange, red cresol, and bromothymol blue) in organic solvents (acetone and methanol) at different gamma doses and different temperatures to propose them as possible dosimeters for low-temperature applications. For this purpose, organic dissolutions were irradiated with gamma rays in the kiloGray (kGy) range at 77 and 295 K, and the color bleaching of the solutions was followed spectrophotometrically (UV-Vis range). The response curves at different temperatures show the linear range interval from 10 to 40 kGy with correlation coefficients of 0.999 and 0.998 for some systems. This is the main reason to continue carrying out studies that allow the proposal of these systems as chemical dosimeters.

## 1. Introduction

Quantitative study in radiation chemistry requires knowledge of the amount of energy absorbed from the ionizing radiation. Determination of this absorbed energy is carried out by using a dosimeter [1]. Dosimeters can be divided into primary (physical) dosimeters, which directly assess the absorbed dose by measuring a physical change, and secondary (chemical) dosimeters, which are the most used and in which a chemical change is related to the received dose [2]. Some commercial applications require a reliable, low-temperature dosimeter for use under the conditions of the irradiation process; for example, (1) for food preservation, such as the irradiation of sea products [3]; (2) radiation processing at low temperature for increasing the efficiency of polymerization reactions for nanoparticles and polymers synthesis [4]; (3) radiation chemical experiments connected to chemical evolution in early systems [5]. Organic dyes that are usually colored compounds on aqueous aerated acidic or alkaline samples have been investigated and used as potential chemical dosimeters [6-8]. Results of some experimental works have proposed using solutions of certain dyes in organic solvents as dosimetry systems that may be measured using spectrophotometer techniques [9-11]. However, the behavior of these systems at low temperatures has not been studied to be able to propose them as dosimetric systems

that work at low temperatures. The aim of the present work is to investigate the response of the change in the absorbance versus absorbed gamma dose in the kiloGray range of 295 and 77 K for some dyes in organic solvents to propose them as chemical dosimeters for low-temperature processes.
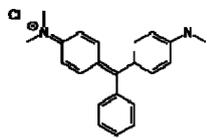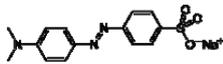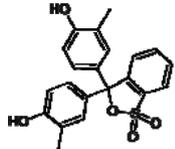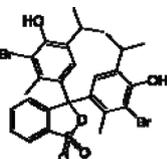
## 2. Materials and methods

### 2.1 Dyes and Organic Solvents

Dyes used were (1) green malachite ($C_{23}H_{25}ClN_2$), (2) methyl orange ($C_{14}H_{14}N_3O_3Na$), (3) red cresol ($C_{21}H_{18}O_5S$), and (4) bromothymol blue ($C_{27}H_{28}Br_2O_5S$). Organic solvents used were (1) methanol ($CH_4O$) and (2) acetone ($C_3H_6O$). All compound were the highest purity available, they were purchased from Sigma-Aldrich and were used without further purification. Solutions of the dyes were prepared using methanol and acetone. To build the calibration curves, several different concentrations were used for each dye ($1 \times 10^{-3}$, $7.5 \times 10^{-4}$, $5 \times 10^{-4}$, $2.5 \times 10^{-4}$, $1 \times 10^{-4}$, $5 \times 10^{-5}$, and $1 \times 10^{-5}$ M).

### 2.2 Irradiation Procedure

Six mL of organic solutions of dyes ($2.5 \times 10^{-4}$ M) were placed in a plastic tube inside a Dewar flask at different

**Table 1.** Linear range data of the absorbance–concentration relationships and molar extinction coefficients of different dye solutions.

| Dye | Molecule structure | Organic solvent | Maximum Wavelength (nm) | Concentration range (M) | Molar extinction coefficient (M$^{-1}$cm$^{-1}$) |
|---|---|---|---|---|---|
| Green malachite |  | Methanol | 427 | $1 \times 10^{-5} - 2.5 \times 10^{-4}$ | 11244 |
| ($C_{23}H_{25}ClN_2$) | | Acetone | 427 | $1 \times 10^{-5} - 5 \times 10^{-4}$ | 11789 |
| [a]Methyl orange ($C_{14}H_{14}N_3O_3Na$) |  | Methanol | 328 | $1 \times 10^{-5} - 5 \times 10^{-4}$ | 7313 |
| Red cresol |  | Methanol | 273 | $1 \times 10^{-5} - 7.5 \times 10^{-4}$ | 13338 |
| ($C_{21}H_{18}O_5S$) | | Acetone | 391 | $1 \times 10^{-5} - 1 \times 10^{-3}$ | 483 |
| Bromothymol blue |  | Methanol | 328 | $1 \times 10^{-5} - 2.5 \times 10^{-4}$ | 9072 |
| ($C_{27}H_{28}Br_2O_5S$) | | Acetone | 399 | $1 \times 10^{-5} - 2.5 \times 10^{-4}$ | 6900 |

[a] Methyl orange is not soluble in acetone under working conditions.

temperatures, at room temperature (295 K) and liquid nitrogen temperature (77 K), in the presence of oxygen. The Dewar flasks were exposed to gamma-irradiation from a $^{60}$Co gamma-ray source (Gammabeam 651 PT facility at Instituto de Ciencias Nucleares, UNAM). The samples were irradiated at different doses. The absorbed doses were between 0 and 40 kGy at a fixed position with a dose rate of 187 Gy/min. The dose rate was determined using the ferrous ammonium sulfate-cupric sulfate dosimeter [12].

## 2.3 Analysis After Irradiation Procedure

After irradiation, the Dewar flask was thermally equilibrated for at least 60 min to analyze aliquots of 4 mL of the irradiated solutions using UV-Vis spectrophotometer Varian Cary 100 Scan at different wavelengths according to the particular dye (Table 1) and using quartz cells with 1 cm optical path lengths.

## 3. Results and Discussion

Applying Beer's law, the molar extinction coefficient for each dye in the different organic solutions was calculated (Table 1). A linear relationship between the dye concentrations and the corresponding absorbance of the solutions at the maximum wavelength was found with a correlation coefficient between

0.999 and 0.998 for some of the dye systems used. With the molar extinction values obtained, the concentration of the dyes selected for the radiolysis experiments was $2.5 \times 10^{-5}$ M.

## 3.1 Gamma Irradiation of Organic Dye Solutions at 295 and 77 K

In this work, a series of dye solutions in methanol and acetone ($2.5 \times 10^{-4}$ M) were irradiated at different absorbed doses (until 40 kGy) and different temperatures (295 and 77 K). The results of the gamma irradiation experiment are shown in Figure 1 for green malachite, in Figure 2 for methyl orange, in Figure 3 for red cresol, and in Figure 4 for bromothymol blue. The data in Table 2 show the response ranges obtained by the plot of the recovery percentage after a 40 kGy adsorbed dose. The temperature effect in radiolysis experiments is also shown in Table 2. When the temperature is raised from 77 K to 295 K, the recovery percentage decreases, most likely because at low temperature the probability of recombination of the primary radicals increases, whereas the mobility of free radicals decreases considerably.

All the studied dyes presented a linear response absorbance change versus absorbed dose irradiation, and this response was taken as an indication of the suitability of any of the used dye systems as a chemical dosimeter. The
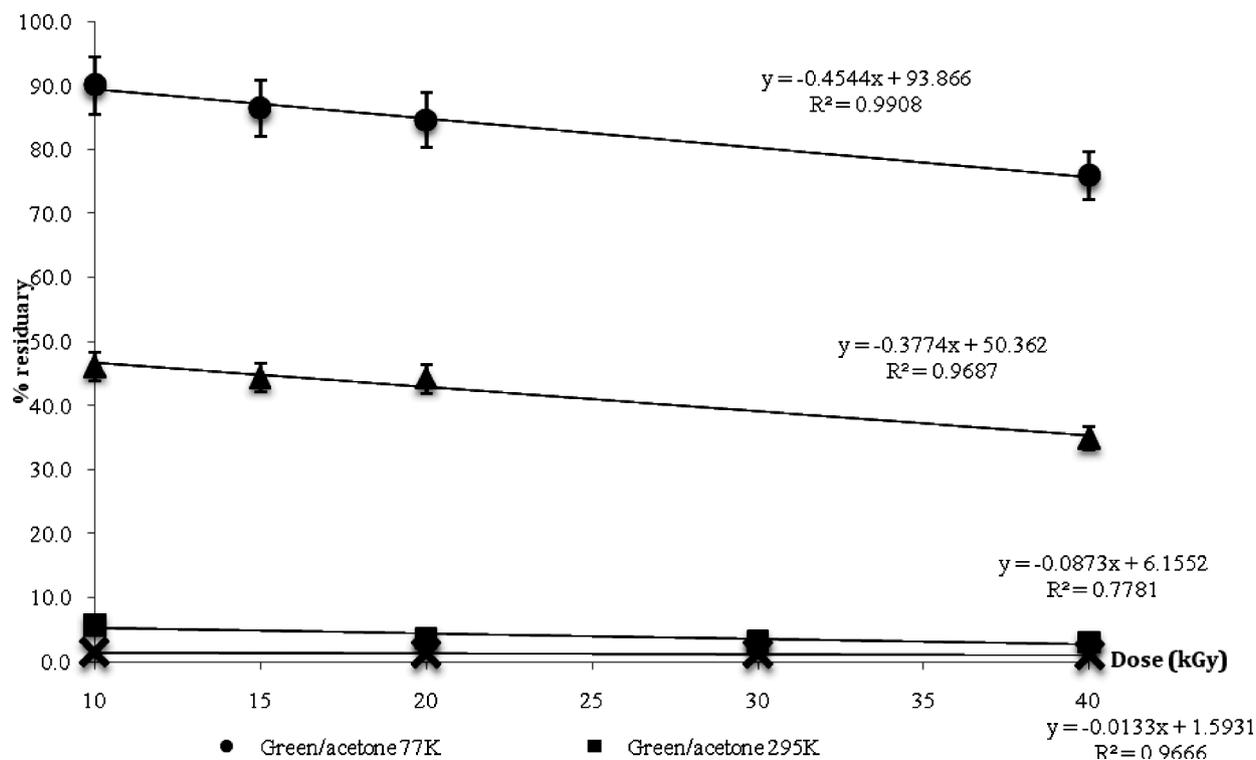
**Figure 1.** Radiolysis of green malaquite in acetone and methanol at 295 and 77 K.

**Table 2.** General results on the irradiation of dyes in organic solution at different temperatures and % residuary after 40 kGy adsorbed dose.

| Dye | Organic Solvent | Correlation coefficient of radiolysis at different temperature | | % Residuary of dye after 40 kGy adsorbed dose | |
|---|---|---|---|---|---|
| | | **295 K** | **77 K** | **295 K** | **77 K** |
| Green malaquite | Methanol | 0.96663 | 0.96865 | 1 | 35 |
| | Acetone | 0.77815 | **0.99075** | 3.1 | 76 |
| Methyl orange | Methanol | 0.95558 | **0.99474** | 20 | 70 |
| Red cresol | Methanol | **0.99827** | 0.59214 | 64 | 77.5 |
| | Acetone | 0.54841 | **0.99938** | 11 | 34 |
| Bromothymol blue | Methanol | **0.99847** | 0.93858 | 24 | 72 |
| | Acetone | 0.77892 | 0.91967 | 10 | 69 |

variations of the recovery percent as a function of doses and temperatures are graphically represented in the following graphs (Figure 1-4). With the values shown in Table 2 of the correlation coefficients closest to 1, it can be determined which systems can be used as chemical dosimeters at 295 and 77 K (Figure 5-6). More studies are needed to understand the effects of the solvent in the irradiated systems. The electronic density of the dyes is much higher than for acetone and methanol, so even though the solutions are diluted, a direct action of the radiation may be important. However, species formed by the radiolysis of the organic solvent may contribute to the degradation of the dyes and range of linearity.

## 4. Remarks

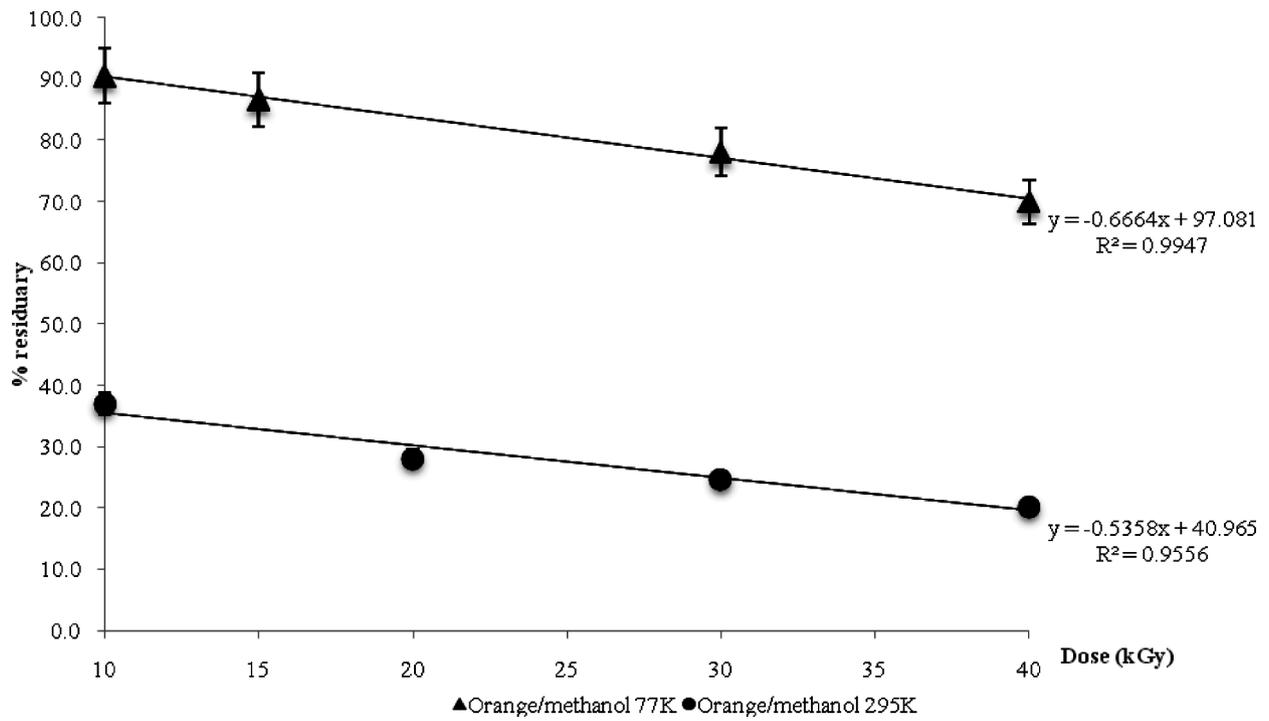We studied the response of some dyes in organic solvents to gamma irradiation at room temperature (295 K) and at low

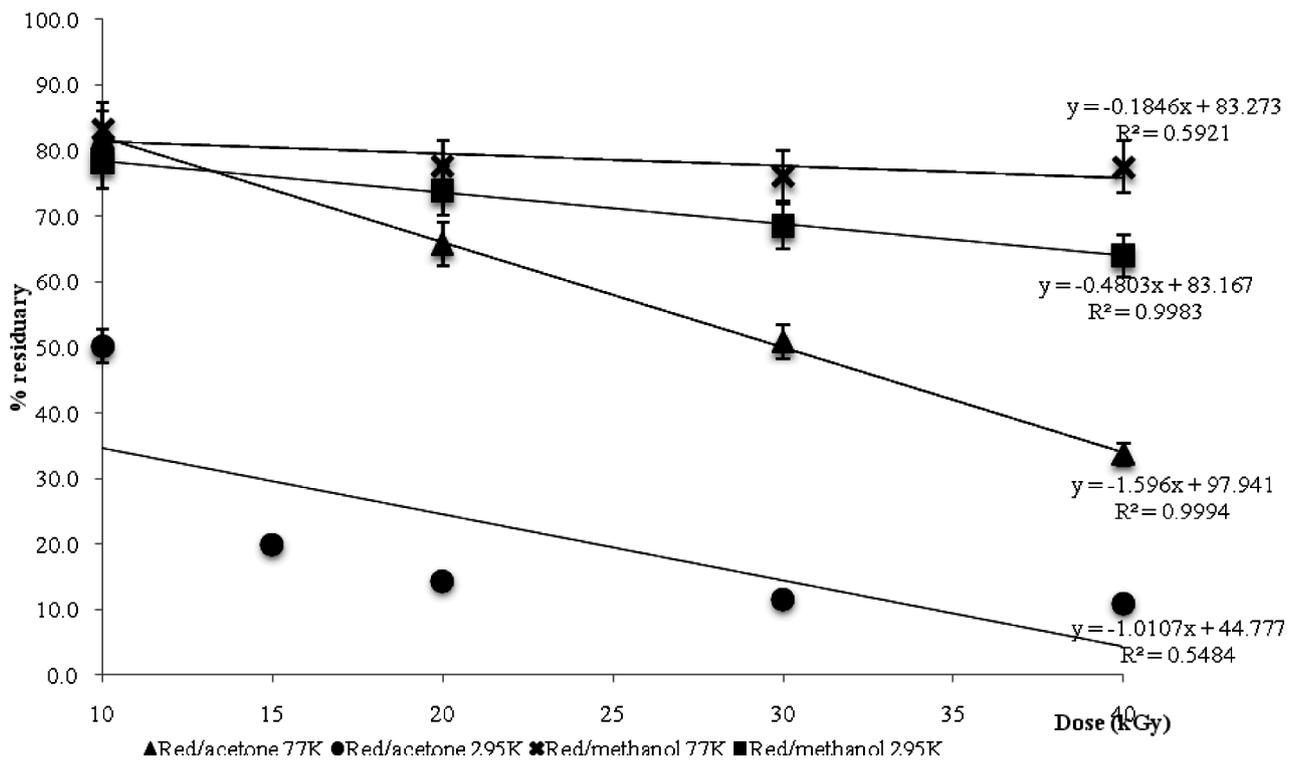**Figure 2.** Radiolysis of methyl orange in methanol at 295 and 77 K.



**Figure 3.** Radiolysis of red cresol in acetone and methanol at 295 and 77 K.
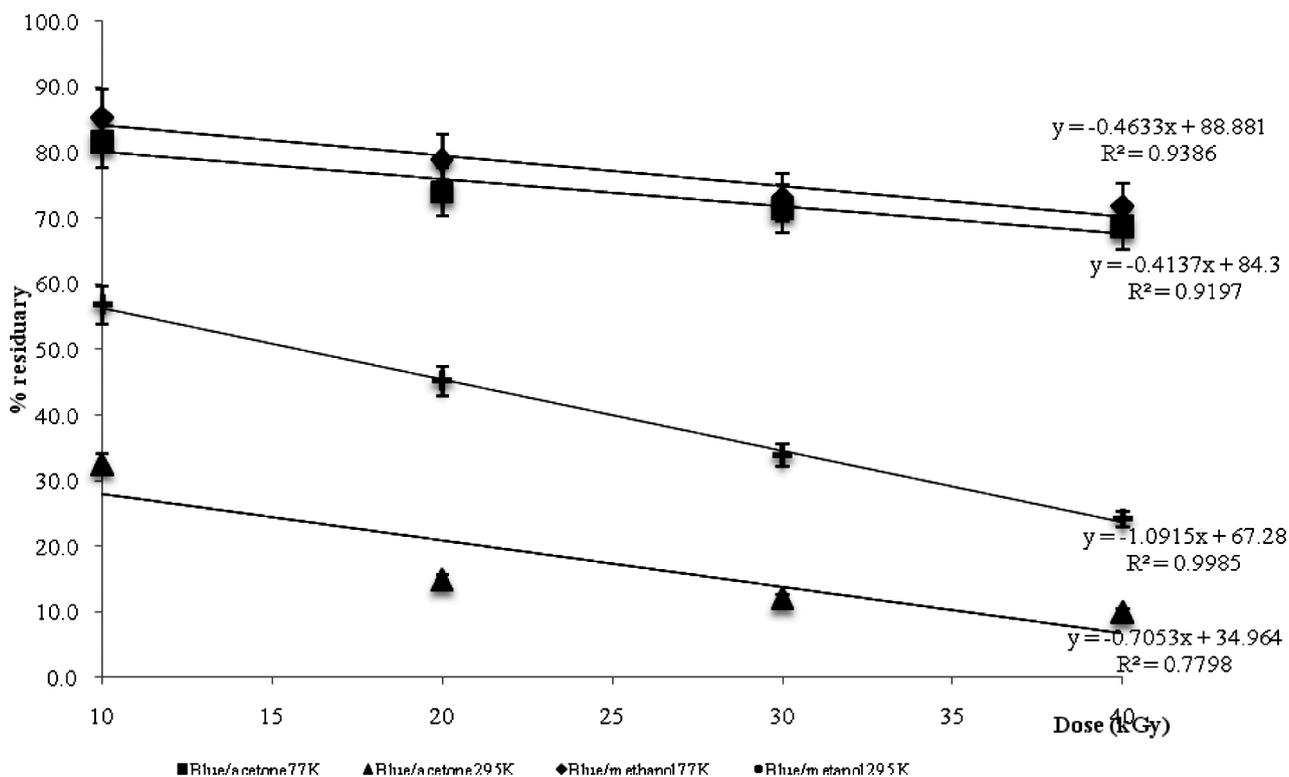
**Figure 4.** Radiolysis of bromothymol blue in acetone and methanol at 295 and 77 K.
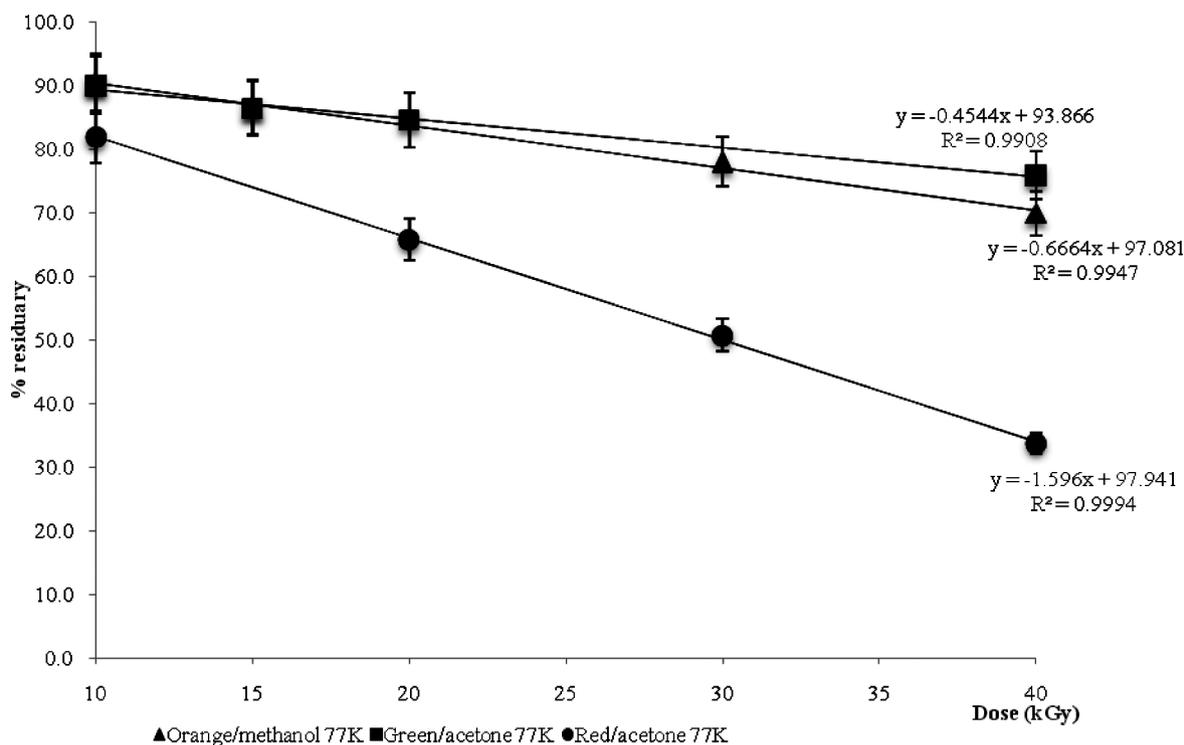


**Figure 5.** Methyl orange/methanol, green malaquite/acetone, and red cresol/acetone are systems that could be used as gamma dosimeters at 77 K.
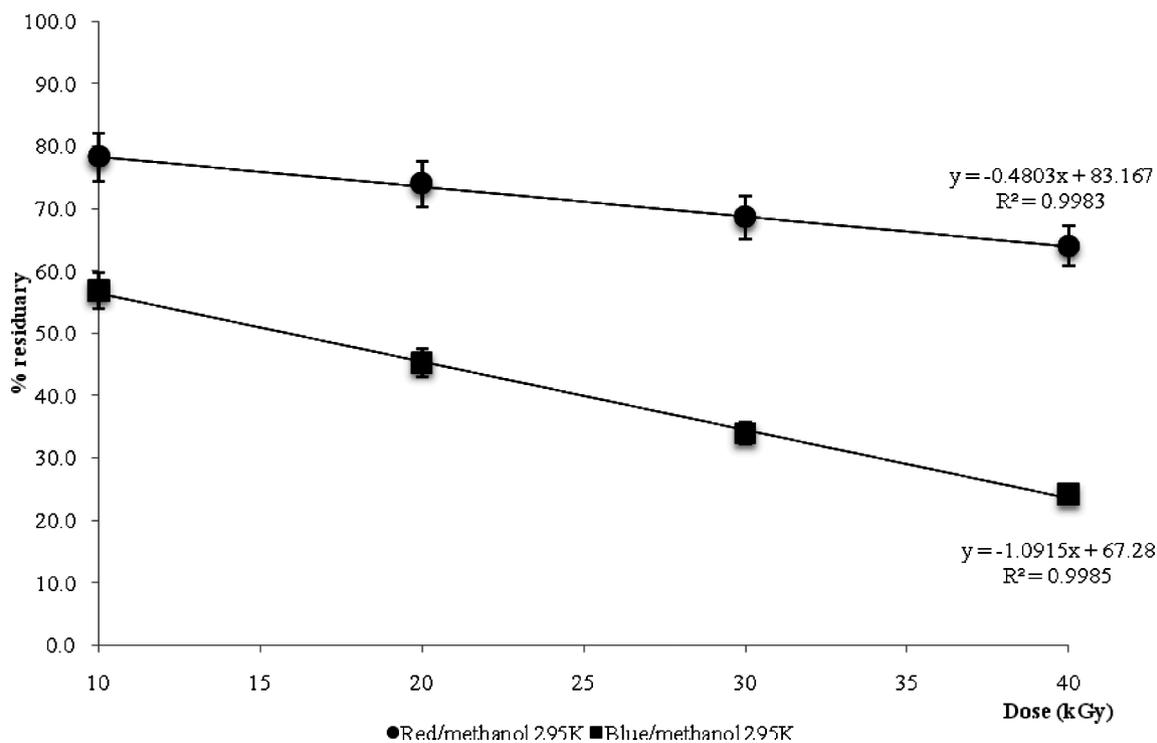
**Figure 6.** Red cresol/methanol and bromothymol blue/methanol are systems that could be used as gamma dosimeters at 295 K.

temperature (77 K). When irradiation takes place at 77 K, the bleaching of the dye is low compared to the bleaching at a higher temperature (295 K), which is an advantage for the dosimetric objectives at low temperatures. The dose–response curve showed linear behavior at 77 K from 10 to 40 kGy for the systems under study. These systems have some advantages over other dosimeters at low temperatures, mainly because they are very simple and easily handled. Moreover, their determination is fast and by UV-Vis spectroscopy, they are not sensitive to sunlight, and they are inexpensive. However, more parameters should be evaluated for their use as low-temperature dosimeters.

## Acknowledgements

## References

[1] F. Attix, *Introduction to Radiological Physics and Radiation Dosimetry* (Wiley-VCH Verlag GmbH & Co, Weinheim, 1986). https://doi.org/10.1002/9783527617135

[2] J. O'Donnell and D. Sangster, *Principles of Radiation Chemistry* (Edward Arnold, United Kingdom), (1970).

[3] F. Diehl, *Safety of irradiated food* (Marcel Dekker, New York), (1995).

[4] S. Lansdowne, R. Gilbert, D. Napper and D. Sangster, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry In Condensed Phases* **76**, (1980).

[5] A. Negron-Mendoza, S. Ramos-Bernal, M. Colin-Garcia and A. Heredia, *RAD Association Journal* (2016).

[6] W. Mclaughlin and M. Desrosiers, *Radiation Physics And Chemistry* **46**, (1995).

[7] M. Rauf and S. Ashraf, *Journal of Hazardous Materials* **166**, (2009).

[8] A. Swallow and A. Charlesby, *Radiation Chemistry of Organic Compounds* (Elsevier Science, Burlington), (2013).

[9] M. Barakat, K. El-Salamawy, M. El-Banna, M. Abdel-Hamid and A. Abdel-Rehim Taha, *Radiation Physics and Chemistry* **61**, (2001).

[10] S. Gafar, M. El-Kelany and S. El-Shawadfy, *Journal Of Radiation Research and Applied Sciences* (2018).

[11] B. Gupta and E. Hart, *Radiation Research* **48**, (1971).

[12] J. Spinks and R. Woods, *An Introduction to Radiation Chemistry* (Wiley, New York), (1990).