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High Dose Film Dosimeter Based on a Mixture of m-cresol Purple and Tetrabromo phenolphthalein Ethyl Ester Dyed Poly (vinyl alcohol)

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Gathering two pH indicator dyes m-cresol purple (MCP), tetrabromophenolphthalein ethyl ester (TBPE), previously studied as individual dosimeter each at low dose application in the same polymer matrix (PVA) extends the application dose response to 60 kGy. This flexible plastic film changes its colour from green to red passing through yellow colour on exposure to γ-rays photons due to the consequent lowering of pH caused by HCl generated from the radiolysis of chloral hydrate. Effect of different concentrations of chloral hydrate on response of the film was investigated. The film shows excellent stability before and after irradiation. The film has excellent stability in 10% to 50% relative humidity range (RH). The overall combined uncertainty (at 2σ) associated with measurement of response (A_i/ A_0) at 438nm for dose range 5-60kGy is 6.33 %. So this film has the ability to monitor the absorbed dose in low and moderate irradiation dose due to its excellent stability before and after irradiation with a significance confidence level.

Keywords: Tetrabromophenolphthalein ethyl ester, m-cresol purple, radiation dosimetry.

Radiation indicators used for identification of irradiated and un-irradiated products in radiation sterilization and food irradiation based on induced colour change by radiation. Due to chemical and physical changes caused in the exposed materials by ionizing radiations (Basfar, 2012) and their sensitivity towards various influence factors (dose rate, light, humidity, temperature etc.), (Shaheen *et al*., 2013), they are not used for quantitative dose measurements while label dosimeters may be used for quantitative dose measurements during radiation processing. These indicators may be labels, papers, inks, which

undergo a visual colour change when exposed to ionizing radiation. These indicators based mainly on radio chromic dye (Kovacs *et al*., 2000). Other based on the pH indicator dye (Abdel- Fattah *et al.*, 1996).

A new radiation sensitive indicator consisting of poly (vinyl alcohol) film containing pH-indicating dye and water soluble chlorine substance (Abdel Fattah *et al*., 1995) was studied. Several polymeric materials in the form of thin films have been successfully developed and used as dosimeters for routine use in gamma rays as well as electron beam radiation processing. Representative examples are radio chromic plastic films of various types (Abdel Fattah and Miller, 1996), Cellulose triacetate (Abdel Rehim *et al*., 1996), Gofchromic dosimetry media (Chu *et al*., 1990) and thin dyed polymeric films (Mclaughlin 1992). Based on the idea of mixing two dyes having different sensitivities to radiation in polymeric substrate were investigated (Abdel Rehim *et al*., 1995).

Radiation bleachable organic dyes were widely investigated (Ebraheem *et al*., 2005). For dose monitoring in radiation processing, the polymeric dyed flexible films are considered to be most commonly used as dosimeters and indicators (Abdel Rehim and Abdel Fattah, 1993) for monitoring the absorbed dose delivered by electron beams and gamma rays (Kovaces *et al*. 2002).

Ueno (1988) developed a radiation dosimeter from acid indicators by coating a high Molecular weight (MW) polymer support (e.g. polyester film) with a composition containing a halogen containing polymer (e.g. PVC), a pigment which changes colour with the changes of pH. A chlorine-containing polymer is not necessary for this radiation to occur.

In the current work, thin films of PVA dyed with TBPE-MCP was investigated to be used as dosimeters for radiation processing.

Experimental

Preparation of stock solution of TBPE-MCP

Preparation of stock solution of TBPE

The stock solution of the indicator was prepared by dissolving 0.05g of TBPE ($C_{22}H_{14}Br_4O_4$ M.W= 661.96 g\ mol) (Sigma-Aldrich, Inc., USA) in 50 ml ethanol.

Preparation of stock solution of m-cresol purple

The stock of sodium salt of the indicator was prepared by dissolving 0.04g of m-cresol purple indicator (product of E. Merk) in 1.1 ml aqueous NaOH {[NaOH= 0.1 mol\ l]} and then the volume was completed by ethanol in a 25ml volumetric flask.

Preparation of TBPE-MCP Films

Films were prepared by dissolving 5g of PVA powder (average MW= 25000) fully hydrolysed 99-100% (product of G.T baker chemical Co. USA) in 100ml double distilled water at about 60^0C, the solution was kept well stirred for about 48h, then left to cool. To each 24ml of PVA 1ml, 2ml & 3ml of TBPE were added and fixed concentration of MCP (3ml). Also 0.1g, 0.2g and 0.3g chloral hydrate was added on fixed combined concentration of 3ml from both of TBPE and MCP and 24ml of PVA to study the effect of both dye concentration and chloral hydrate concentration on behaviour of dosimeter response. After preparing the six films, they were kept well stirred at room temperature for about 3hr's in order to obtain a uniformity mixed solution. Each solution was poured on a 15x15 cm^3 horizontal glass plate, dried at room temperature for about 48h. After drying, the films were stripped from the glass plate, then cut into 1x1cm^2 pieces and stored for further investigation. The thickness of the obtained films was found to be 0.049± 0.005mm (1δ).

Apparatus

The absorption spectra of the un-irradiated and irradiated films were measured throughout the wavelength range (200-800nm) using a UVKON 860 spectrophotometer. The film thickness was measured using a Digitrix-Mark thickness Gauge (precision≠1um; 1δ).

Irradiation was carried out with gamma rays using Gamma cell-220 Excel ^{60}Co irradiation facilities (Manufactured by MDS Nordian, Canada). The absorbed dose rate in water was measured by Frike dosimetery to be {G(Fe^{+3}= 2.35161 kGy/h)}. The temperature during gamma ray irradiation was 30^0C, and the electronic equilibrium conditions were maintained during irradiation through keeping the films between two polystyrene slabs of 3mm thickness.

Results and Discussion

Absorption Spectra

The absorption spectra for the film TBPE-MCP from previous study (El- Kelany, 2011) shows a main absorption band in visible region characteristic of a blue peaking for TBPE/ PVA at 606nm. Amplitude of this band decreases gradually with the increase of absorbed dose of gamma ray photons. The film change its colour from blue to green and finally to pale green in presence of HCL source, and the useful dose range was found to be in the range 1-5 kGy. Also the absorption spectra of MCP/ PVA films from previous study **(**Eid, 2008**)** shows a main absorption band in the visible region characteristic to the yellow peaking at 417nm. The amplitude of the absorption band decreases and shifts to lower wavelength with the increase of absorbed dose and a new absorption band, peaking at 521nm characteristic of a red colour is formed and its amplitude increases gradually with the increase of absorbed dose. The radiation induced colour change of these films from yellow (the alkaline form of MCP) to red (the acidic form of MCP) indicating acid formation. The useful dose range was found to be in the range of 2-6kGy.

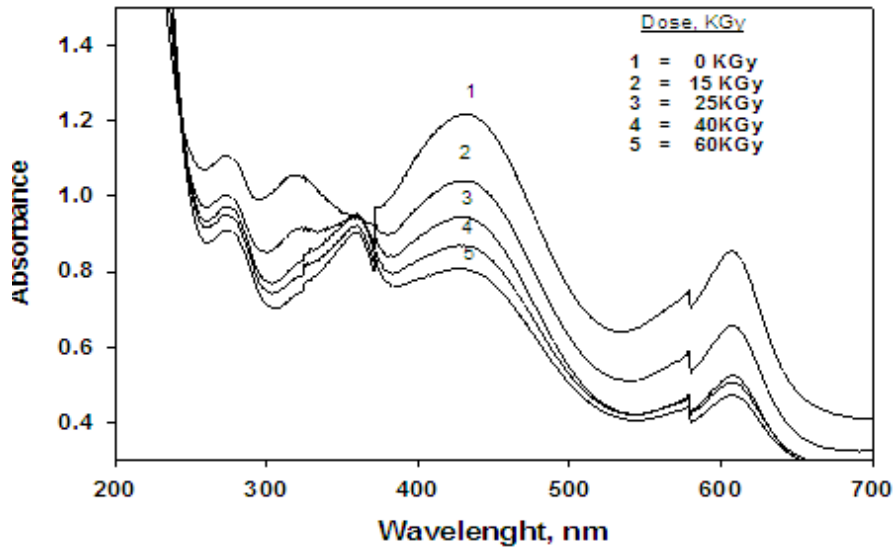

Fig. 1.a The absorption spectra of TBPE, MCP/ PVA films un-irradiated and irradiated to different doses without chloral hydrate.

In the current work, gathering the two above mentioned dyes in the same polymer matrix as TBPE, MCP/PVA extend the dose range up to 60kGy for serving high dose application. Fig. 1a.& 1b. shows the absorption spectra of the un-irradiated and irradiated films measured throughout the wavelength range (300-700nm). The absorption spectra of the TBPE, MCP\ PVA (0.2 phr TBPE, 0.32 phr MCP) without chloral hydrate recorded before and after irradiation to different doses.

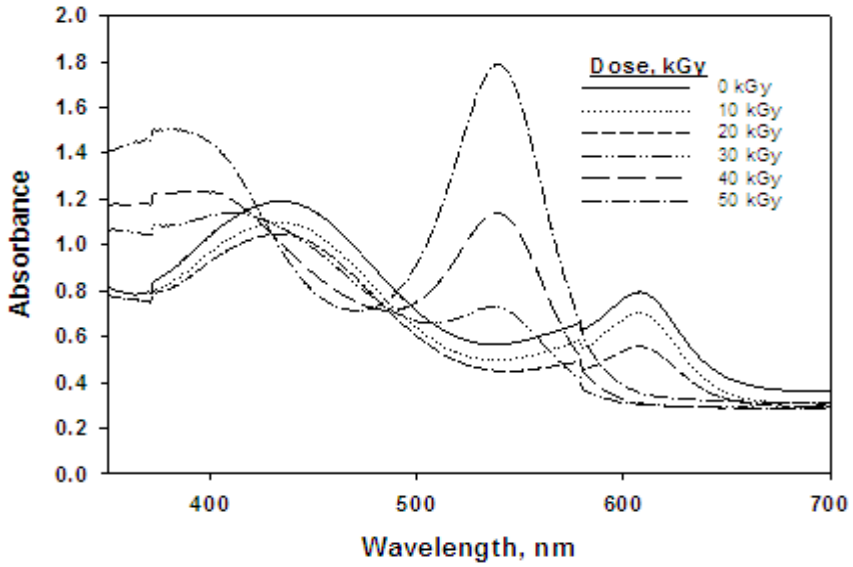

Fig. 1b. The absorption spectra of TBPE, MCP/ PVA films un-irradiated and irradiated to different doses with chloral hydrate.

The absorption spectrum of un-irradiated film shows a main absorption band in the visible region characteristic of a blue colour peaking at 606nm, and another absorption band at 438nm characteristic of a yellow colour peaking. The green colour is observed due to the visual sensation of mixed ratios of dyes. On irradiation we noticed more significance sensitivity for MCP in comparison with TBPE towards the absorbed dose but no peak observed in the red range due to absence of HCl source (still alkaline phase). In the presence of chloral hydrate (16.6 phr), We noticed decrease in the intensity of MCP and TBPE with increase of absorbed dose. A new absorption band, peaking at 538nm characteristic of a red colour is formed, its amplitude increases with the increase of absorbed dose.

The radiation-induced colour change of these films from green colour to red colour through intermediate yellow colour indicates acid formation. The dose at which the red colour appears depends on the concentration of both dyes and chloral hydrate in the film. Fig. 2. shows the response curve of TBPE, MCP\ PVA containing 0.2 phr TBPE, 0.32 phr MCP and 16.6 phr chloral hydrate. It can be noted that the curve have S-shape characteristic of pH indicator phenomena in acid-base titration. The figure shows the response curve in terms of optical density after irradiation (A_i) to optical density before irradiation (A_0) at 438nm. The curve shows the useful dose range extends up to 60 kGy. So the presence of both dyes together transfer the response from limited application in low doses to more wide application covering the low and intermediate dose range. These phenomena may be due to dissociation takes place for the absorbed dose between both two dyes having different sensitivity which leads to extend the dose range.

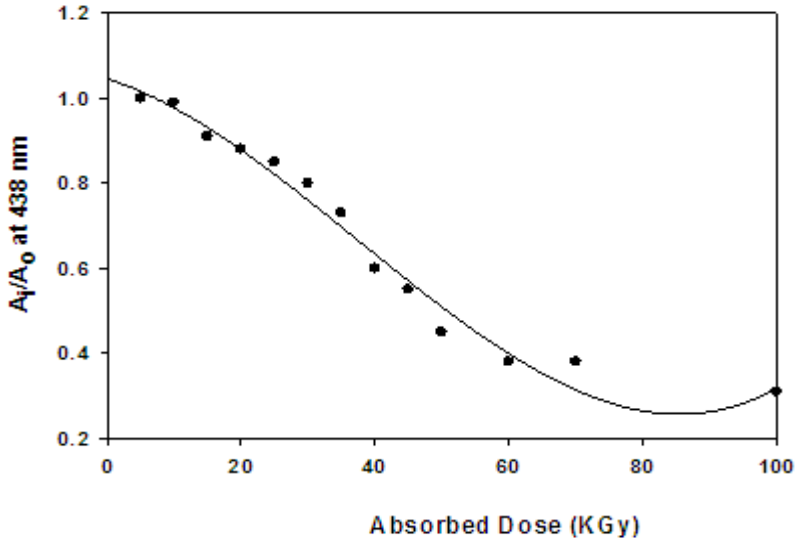

Fig. 2. Change of A_i\ A_0 at 438nm as a function of absorbed dose of 0.2phr TBPE, 0.32 phr MCP\ PVA films. (16.6phr chloral hydrate).

Fig. 3. shows the response curve of TBPE, MCP\ PVA film containing different concentration of dyes 0.06phr, 0.13phr, 0.2phr TBPE and 0.32phr MCP and fixed concentration of chloral hydrate (16.6phr). It can be seen that all curves have the same trend and reaches saturation at doses proportional to the concentration of TBPE dye.

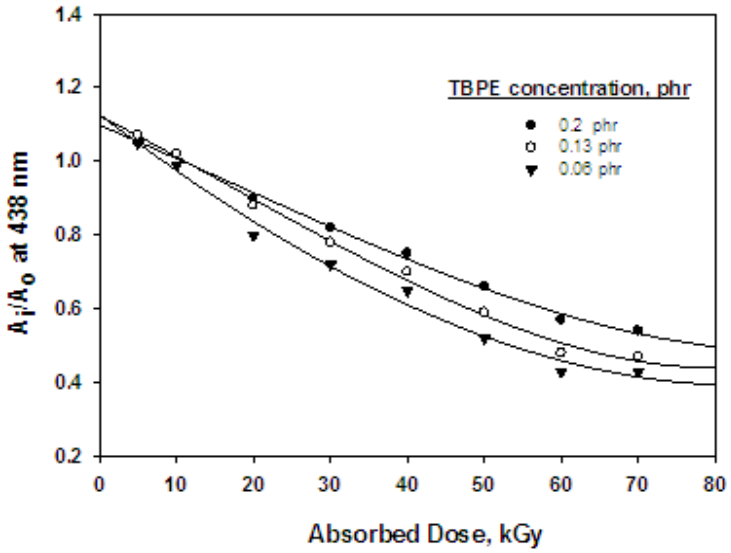

Fig. 3. Change of Ai/ Ao as a function of absorbed dose of TBPE, MCP/ PVA films with different concentrations of TBPE dye.

Fig. 4. shows the response curve of TBPE, MCP\ PVA film containing different concentrations of chloral hydrate and fixed concentrations of dyes (16.6phr, 33.2phr, 49.8phr). All curves shown in figure have the same trend but differ in the slope value (slope of initial part of curves). The slope increases with increase chloral hydrate values.

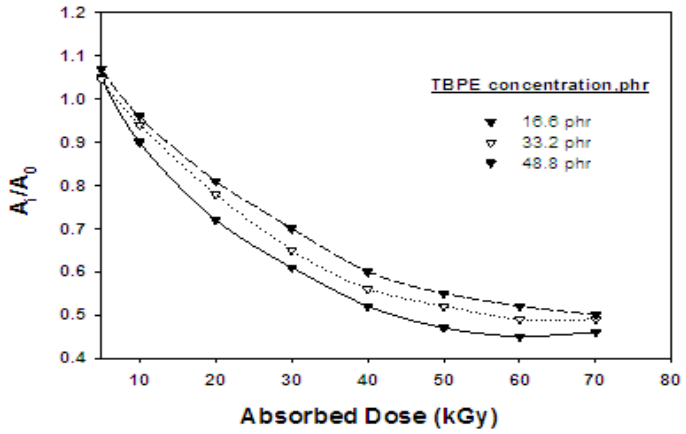

Fig. 4. Change of Ai/ Ao as a function of absorbed dose of TBPE, MCP/ PVA films with different concentrations of chloral hydrate.

Humidity during irradiation

The effect of RH during irradiation on the response was investigated by irradiate TBPE, MCP\ PVA films (16.6phr CH), (0.2phr TBPE, 0.32phr MCP) at 438nm by 35kGy at different relative humidity (0%, 11%, 33%, 54%, 76%, 92%). Irradiation was carried out while the films were suspended over various saturated salt solutions in an enclosed jar except for the 0% RH which was embedded over dried silica gel. Fig. 5. shows the variation in optical density after irradiation (A_i) to optical density before irradiation (A_o) as a function of percentage RH during irradiation relative to that at 33%. It was found that, the films have no appreciable effect in the range of RH (10-50%), although the response shows somewhat different sensitivities at both higher and lower humidity.

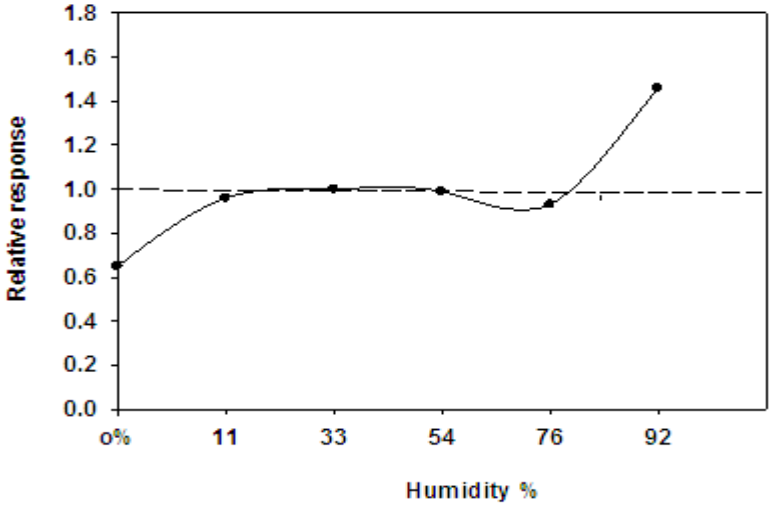

Fig. 5. Variation of relative response of TBPE, MCR/ PVA films as a function of relative humidity during irradiation at 438nm.

Assessment of uncertainties

To be meaningful, a measurement of gamma ray shall be accompanied by an estimate of the uncertainty in the measured value. Factors contributing to the total uncertainty may be separated into two types, type A and type B (ISO\ ASTM, 2002 and Taylor *et al.*, 1994). The first factor is associated mainly with the measuring equipment and the film while the second is mainly related to the calibration. The reproducibility of the UVKON spectrophotometer was determined by reading the absorbance value (at 438nm wavelength and absorbance level 0.8) of irradiated films several times (one hundred readings per

film). From the data obtained, it was found that the coefficient of variation (1σ) is ±0.2%, reflecting the precession of the spectrophotometer. The reproducibility of the measurements of several films (10 times for film) was found to be 1.8% (1 σ). On the other hand, the type "A" uncertainties (at one standard deviation, 1σ) arising during calibration over the useful response range were found to be ± 2.6%. The combined uncertainties (U_c) can be obtained by combining all the components in quadrature at one standard deviation (1σ) as follow:

$$Uc= \sqrt{(0.2)^2+ (2.6)^2+ (1.8)^2}= 3.168$$

The combined uncertainty (at two standard deviations, i.e 2σ, approximately equal to 95% confidence level) is found by multiplication of Uc at (1σ) by two. Hence the combined uncertainty is 6.33%.

Pre-irradiation stability

The colour stability of TBPE, MCP\ PVA films containing (16.6phr chloral hydrate, 0.2phr TBPE, 0.32phr MCP) at 438nm before irradiation were tested by storing the films at 35% RH at room temperature (25± 3^0C) in the dark and under laboratory fluorescent light.

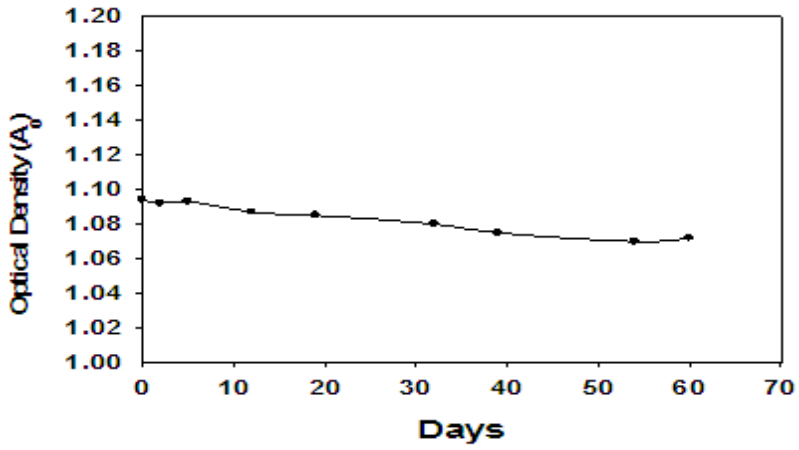

Fig. 6. Post-irradiation stability of TBPE, MCP/ PVA films stored in diurnal cycles of day light at room temperature in 25°C at 438nm.

The absorbance of the films was measured at 438nm wavelength at different time intervals during the pre-irradiation storage period of 60 days. The change in absorbance at 438nm as a function of storage time is shown in Fig. 6. It can be seen that the films have excellent stability, just 2% decrease through 60 days.

Post irradiation stability

The colour stability of TBPE, MCP/ PVA films containing (16.6phr chloral hydrate, TBPE 0.2phr and MCP 0.32phr) at 438nm before irradiation were tested by storing the films at 35% RH at room temperature (25± 3^0C) in the dark and under laboratory fluorescent light. The change in absorbance at 438nm as a function of storage time is shown in Fig. 7. It can be seen that the films have excellent stability, just 2% decrease through 60 days storage time in dark and 4% decrease in light.

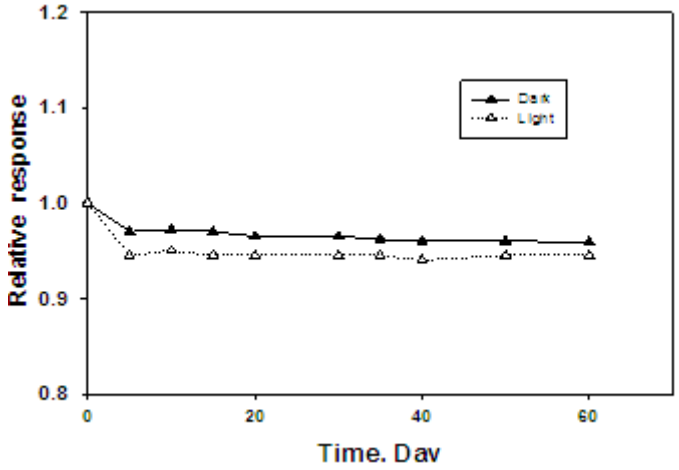

Fig. 7. Post-irradiation stability of TBPE, MCP/ PVA films stored in diurnal cycles of day light at room temperature in 25°C at 438nm.

Conclusion

Films made of PVA dyed with mixed dyes TBPE-MCP are useful radiation dosimeters in the dose range 5-60kGy. The films are highly stable for long times in dark and are not affected by relative humidity changes in the range of (10-60%). These films are easy to make and thus, amenable for large-scale production and application for routine irradiation process of food and medical devices. The combined uncertainty at 2σ using TBPE/ MCP/ PVA films was found to be 6.33%.

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دراسة أمكانية أستخدام خليط من صبغتي الميتاكريزول الأورجوانية و التيترابروموفينول فيثالين اثيل أستر في صبغ أفلام البولي فينيل الكحول لقياس الجرعات الاشعاعية

عصام فهيم ، شاديه عبد المنعم ، محمود عبد الواحد الأهدل

قسم الوقايه و الجرعات الاشعاعيه ، المركز القومى لبحوث و تكنولوجيا الاشعاع ، ص.ب. ٢٩ مدينة نصر ، مصر.

جمع صبغة الميتاكريزول الأرجوانية مع صبغة التيترابرو موفيثالين اثيل أستر (كواشف درجة الحموضة) الذي سبق دراستهم منفردين في قياس الجرعات الأشعاعية منخفضة الجرعة في وسط حاضن وهو مادة البولي فينيل الكحول في صورة فيلم بلاستيكي مرن بغرض زيادة قدرة هذا الفيلم علي قياس الجرعات الأشعاعية المنخفضة و المتوسطة الجرعة و حتي مدي يصل الي ٦٠ كيلوجراي .

هذا الفيلم المرن المحضر معمليا يتغير لونة من الأخضر الي الأحمر مرورا باللون الأصفر عند التعرض لأشعة جاما و ذلك نتيجة تكسير مادة الكلورال هيدرات المضافة للفيلم و تحرير حمض الهيدروكلوريك الذي يخلق وسط حامضي في الفيلم تتأثر بة الصبغتين.

تم دراسة تأثير تركيز الكلورال هيدرات علي منحني الأستجابة كما تم أيضا دراسة تأثير تركيزات الصبغة ، و قد أظهرالفيلم ثباتيه ممتازه قبل و بعد التشعيع وأيضا ثباتيه فى مدى من الرطوبه النسبيه يتراوح ما بين (٥٠-١٠%). و بحساب اللايقين الكلى عند مستوى ثقه (٢ سيجما) المصاحب للقياسات فى مدى من (٥-٦٠) كيلو جراى وجد نسبته ٦.٣٣%.

لذا فهذا الفيلم يمكن أستخدامه في الجرعات المنخفضه و مراقبة عمليات التعقيم في وحدة التشعيع الصناعي (ليبل دوزيمتر) لما يتميز بة من ثباتيه ممتازه قبل و بعد التشعيع و مستوي ثقة مناسب.