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Possible Using of Tetra Bromo Phenol Phthalein Ethyl Ester as a Liquid Dosimeter

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AQUEOUS SOLUTION of pH indicator *Tetrabromo phenol phthalein ethyl ester (TBPE)* containing of chloral hydrate was studied for using as a liquid dosimeter.

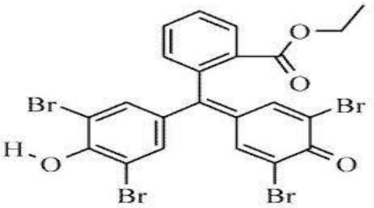
The useful measuring range was found to be of (0.5-2kGy) depending on concentration of both dye and chloral hydrate added.

The dosimeter has good stability before and after irradiation under different storage conditions. Comparison study between direct irradiation of TBPE containing chloral hydrate and back titration of TBPE through irradiation of chloral hydrate was investigated.

Keywords: *Tetrabromo phenol phthalein ethyl ester (TBPE), back titration.*

Many solutions undergo γ-irradiation for effective sterilization such as medical solutions, cosmetic lotions, ointments and others need dose detection. Using liquid dosimeters or labels, the absorbed doses were detected without any absorption extension coefficient corrections. Many radiation sensitive indicators for qualitative dose measurements have been manufactured to distinguish processed units from unprocessed irradiation units (Abdel-Rehim and Abdel-Fattah, 1993 and Abdel-Rehim *et al.,* 1996). These indicators may be labels, papers and inks which undergo a visual colour change when exposed to ionizing radiation (Abdel-Rehim *et al.,* 1985). These indicators based mainly on radiochromic dye (Akhavan *et al.,* 2002, Butson *et al.,* 2001 and kovacs *et al.,* 2000). They are not used for quantitative dose measurements while label dosimeters may be used for quantitative dose measurements during radiation processing.

Materials



Scheme 1. Chemical structure of Tetra bromophenol phthalein ethyl ester.

Apparatus

The Gamma chamber 4000 A Co ^{60} irradiation facility (Manufactured at Bhabha Atomic Research Centre, India) is a compact and self-contained irradiation unit. The dose rate at (Feb. 2015) was 2.08kGy/ h.

UV/ VIS spectrophotometer

UV-VIS spectrophotometer used in all measurements was UV/ VIS spectrophotometer UV4 (Product of Unicam Co. Ltd, England).

Experimental

Preparation of stock solution of TBPE and chloral hydrate CH

The stock solution of the indicator was prepared by dissolving 0.05g of TBPE ($C_{22}H_{14}Br_4O_4$, M. W.=661.96g/ mol), Sigma-Aldrich, Inc, USA. in 50ml ethanol. The stock solution of the chloral hydrate was prepared by dissolving 0.3g in 50ml of double distilled water; the solution was stirred for 3h for effective dissolution.

Results and Discussion

Direct irradiation technique

Absorption spectra

The absorption spectra of the unirradiated and irradiated liquid TBPE solutions were measured throughout the wavelength of 300-900nm at different doses without CH as shown in Fig. 1. The absorption spectrum of unirradiated solution shows a main absorption band in the visible region characteristic of a blue colour peaking at 604nm (Fig. 1). The amplitude of this band decreases gradually with the increase of absorbed dose of γ-ray photons.

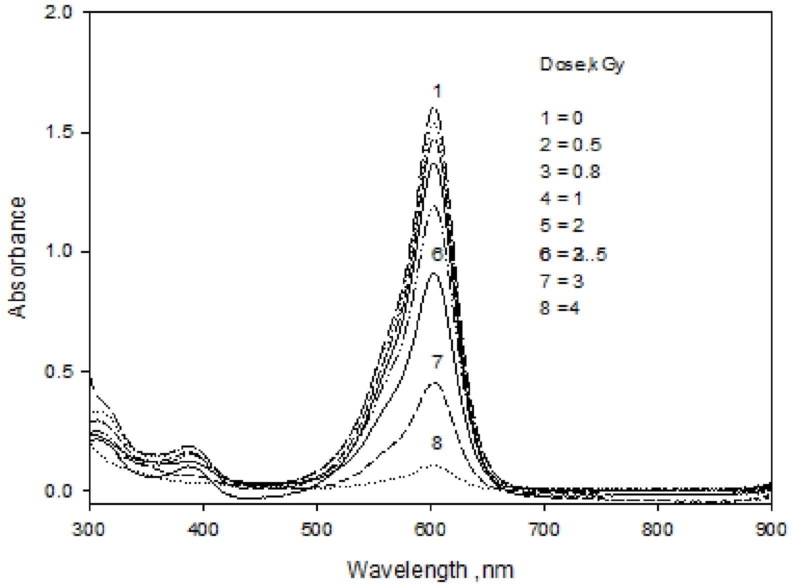


Fig. 1. The absorption spectra of the unirradiated and γ-irradiated TBPE solutions to different absorbed doses, [TBPE]= 0.456µmol/ L.

In presence of 8.77x 10^{-3} mol/ L chloral hydrate, the irradiated TBPE solution shows a main absorption band peaking at 604nm, Fig. 2.

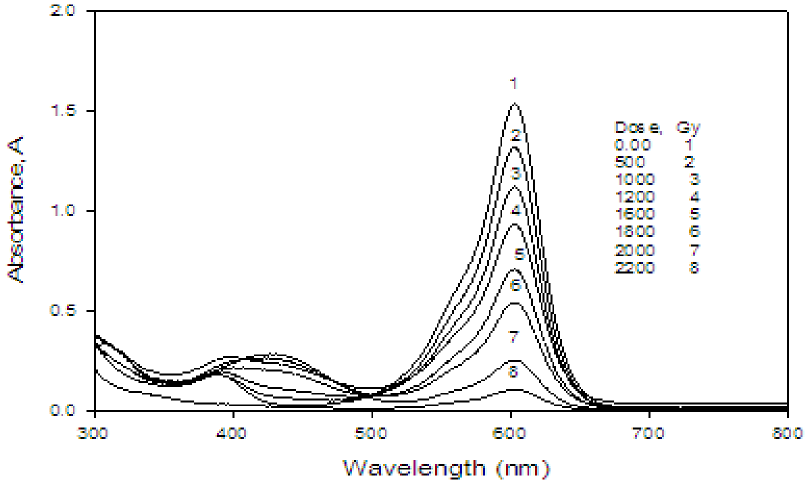


Fig. 2. The absorption spectra of the unirradiated and irradiated TBPE solutions with different doses. [TBPE]= 0.456mol/ L and [CH]= 8.77x 10^{-3} mol/ L.

The amplitude of this band decreases gradually with the increase of γ-rays. Upon irradiation the TBPE solution changes its colour from blue to green and finally to pale green indicating acid formation. The green colour is observed due to the visual sensation of mixed ratios of unchanged part (blue colour) of indicator and changed part (yellow colour resulting from developing broad peak at 430nm). The same behaviour obtained in irradiated TBPE dye in plastic matrix polyvinyl alcohol films (El-Kelany, 2011).

Response curves

Fig. 3. shows the response curves of TBPE solutions containing different dye concentrations of (0.228, 0.456 and 0.684mol/ L). It can be noticed that the three curves have S-shape characteristic of pH indicator in an acid base titration. Each curve reaches saturation at different dose depending on the concentration of TBPE dye. Its show the response curves in terms of change in optical density against absorbed dose, (ΔA)= A_0–A_i, where A_0 and A_I are the values of optical density for the unirradiated and irradiated solutions respectively. The curves show that the dose range extends up to 5kGy.

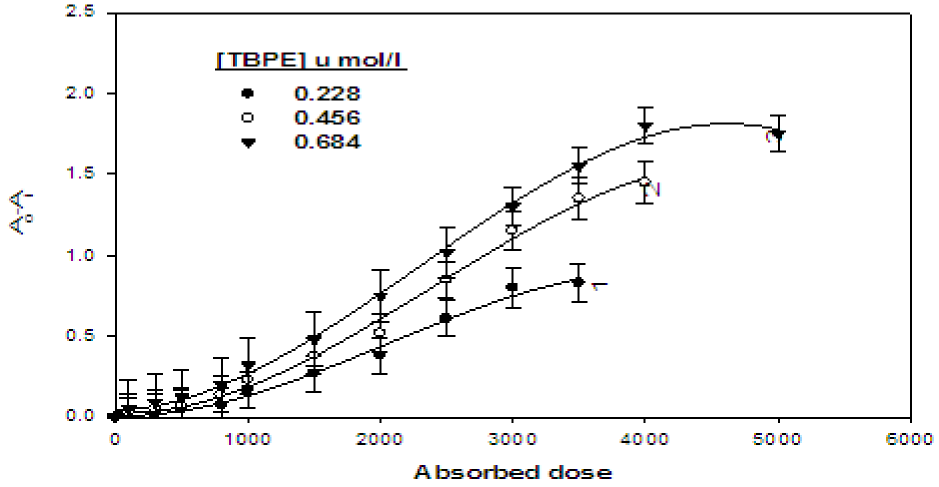


Fig. 3. Change of ΔA, (A0–Ai), at 604nm, as a function of absorbed dose for different TBPE dye concentrations.

Four different CH concentrations 8.77x 10^{-3}, 1.75x 10^{-2}, 2.63x 10^{-2} and 3.5x 10^{-2} mol/ L and the same concentration of dye 0.456mol/ L^{-1} were examined. It was found that the useful dose range of these solutions extend from 100Gy to 2200Gy. It was noticed that the bleaching reaction takes place faster within solutions containing CH than without CH, i. e., CH act as sensitizer.

Fig. 4. shows that the response of solutions containing different CH concentrations (8.77x 10^{-3}, 1.75x 10^{-2}, 2.63x 10^{-2} and 3.5x 10^{-2} mol/ L) was decreased to be ranged from 0.1-2.2kGy, meaning the existence of CH accelerate the degradation of TBPE dye nearly about double fold than that one dose not containing CH. This means that the resulting species produced from the irradiation of CH have a significant effect on the dye degradation. Fig. 5. shows the slope of the linear parts in response curves given in Fig. 3. as a function of TBPE concentrations at absorption band 604nm.

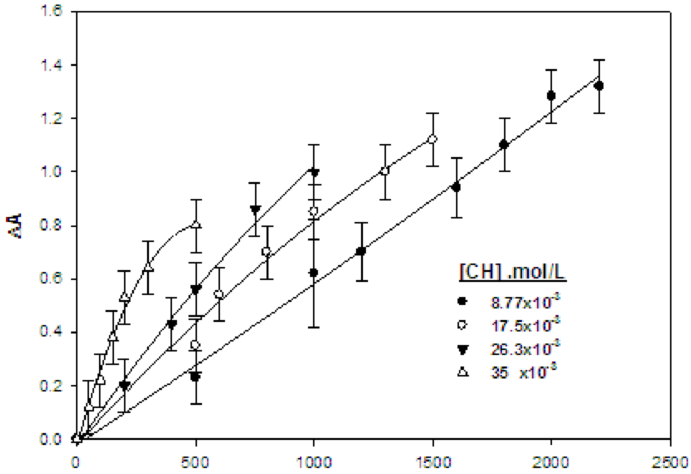


Fig. 4. Change of ΔA, $(A_0 – A_I)$, as a function of absorbed dose for different concentrations of chloral hydrate CH, [TBPE]= 0.456µmol/ L.

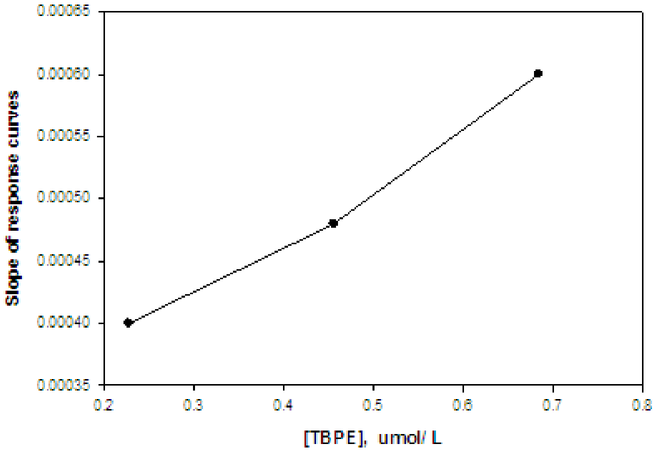


Fig. 5. Radiation sensitivity of TBPE-CH solutions against the concentration of TBPE dye.

Fig. 5. shows the slope of the linear parts in response curves given in Fig. 3. as a function of TBPE concentrations at absorption band 604nm. It can be seen that the radiation sensitivity of TBPE-CH solution increases with increasing the TBPE concentrations.

The radiation chemical yield (G-Value)

The radiation-chemical yield (G-value) defined as the number of moles of dye degraded by the absorption of one J of energy (unit: mole/J). The G-value calculated from the general relation.

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

Where, ΔA is the change in absorbance at ΔA_{max}, b is the optical path length (1cm), ε is the linear molar extension coefficient at ΔA_{max} (L/ mol/ cm), ρ is the density of the dosimeter, 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 $3.2\text{x}\ 10^{-4}$ L/ mol/ cm for TBPE solutions.

The calculated G-value for these solutions was tabulated in Table 1. From the table it could be noticed that the G-value value increase with the increase of the dye concentration and chloral hydrate concentration.

TABLE 1. The calculated G-value for TBPE solutions at different dye and CH concentrations.

TBPE, µmol/ L	CH, mol / L	G-value, µmol/ J
0.228	--	$0.283\text{X}10^{-2}$
0.456	--	$0.62\text{X}10^{-2}$
0.684	--	$1.32\text{X}10^{-2}$
0.456	$8.77\text{X}10^{-3}$	$0.146\text{X}10^{-4}$
0.456	$17.5\text{X}10^{-3}$	$0.252\text{X}10^{-4}$
0.456	$26.3\text{X}10^{-3}$	$0.315\text{X}10^{-4}$
0.456	$35\text{X}10^{-3}$	$0.672\text{X}10^{-4}$

Pre-irradiation stability

The absorbance of the solutions was measured at 604nm wave length at different time intervals during the pre-irradiation storage period of 60days. Excellent stability is obtained for solutions stored in dark and light, 3% and 5%, respectively at the end of storage time as shown in Fig. 6.

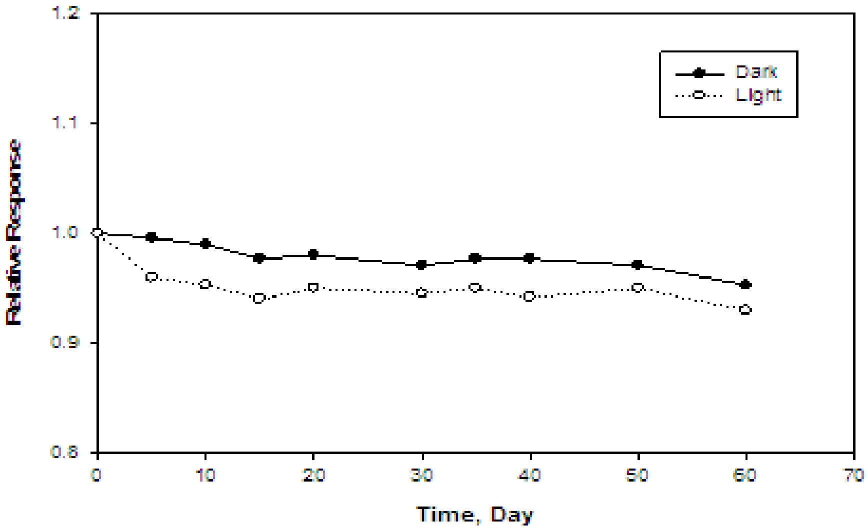


Fig. 6. Pre-irradiation stability of TBPE solutions stored in dark and light at room temperature, as a function of storage time.

Post-irradiation stability

The post-irradiation stability of TBPE-CH solutions have (TBPE= 0.456 mol/ L) and (CH= 8.77x 10^{-3} mol/ L) irradiated to 500Gy is investigated by storing the solutions in the dark at room temperature and in diurnal cycles of day light.

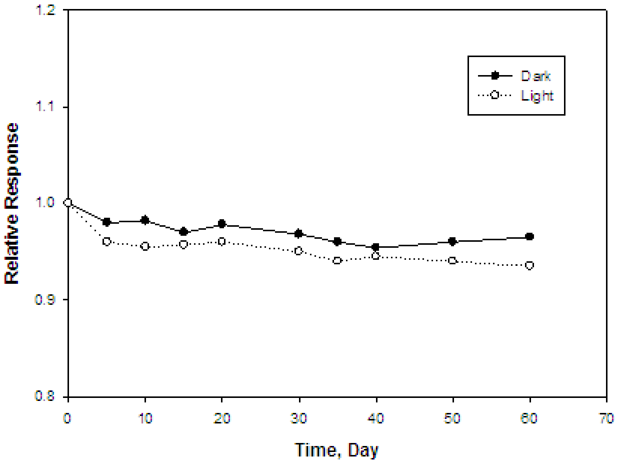


Fig. 7. Post-irradiation stability of TBPE solutions ([TBPE]= 0.456µmol/ L and [CH]= 8.77x 10^{-3} mol/ L) stored in dark and light at room temperature, as a function of storage time at 0.5kGy.

Excellent stability also obtained as pre-stability with overall decrease in relative absorbance by just 2% and 4%, respectively for solutions stored in dark and light through 60days storage period as shown in Fig. 7.

Indirect irradiation technique

Sustain studying this liquid dosimeter was done through avoid exposure TBPE pH indicator dye for γ-radiation directly using back titration technique followed by color measurements using spectrophotometer. Using (1N) chloral hydrate irradiated by γ-irradiation at (0.2, 0.5, 1, 3 & 5kGy) in titration of dye solution (0.1ml of irradiated CH solution with 2ml of dye solution). Fig. 8. shows that the TBPE dye is react with resulting H^+ according to absorbed dose leads to color changes and decrease in peak intensity at 601nm (blue-green-pale green). It was found that the useful dose range of this dosimeter is 1-5kGy.

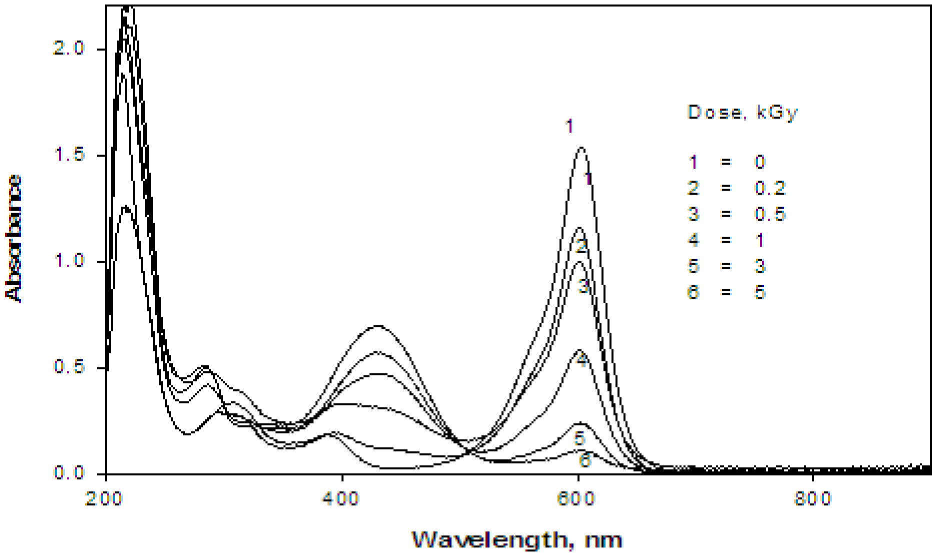


Fig. 8. The absorption spectra of TBPE aqueous solution unirradiated and irradiated to different absorbed dose.

Response curve

Fig. 9. shows the response curve of TBPE dye titrated by different concentration of CH resulting from direct exposure for gamma radiation starting by (0.2kGy to 5kGy). The response was established with the same concentration

of dye used in irradiation of solution containing the same dye mentioned in direct technique, [TBPE]= 0.456µmol/ L.

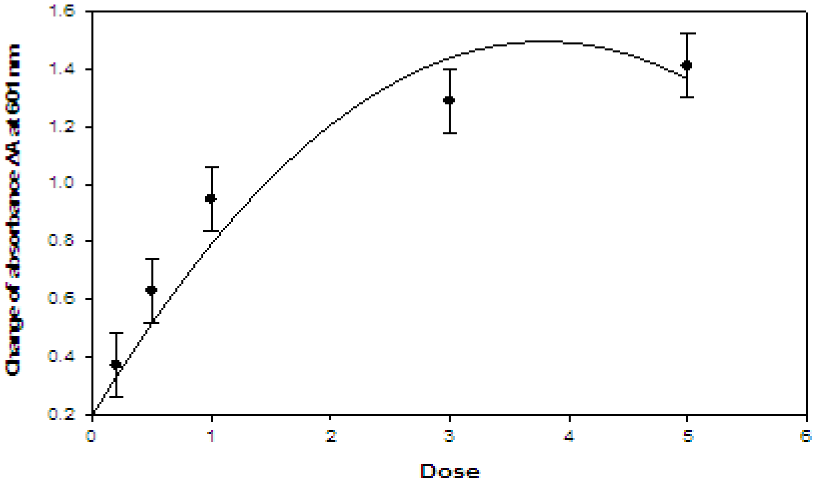


Fig. 9. Change of response of TBPE/ CH solution [Ao-Ai] as a function of the absorbed dose.

Fig. 10. shows the sharp decrease in the pH measured values for chloral hydrates solutions on exposing to γ-radiation till 1kGy, then little bit decrease to the end of the target irradiation period.

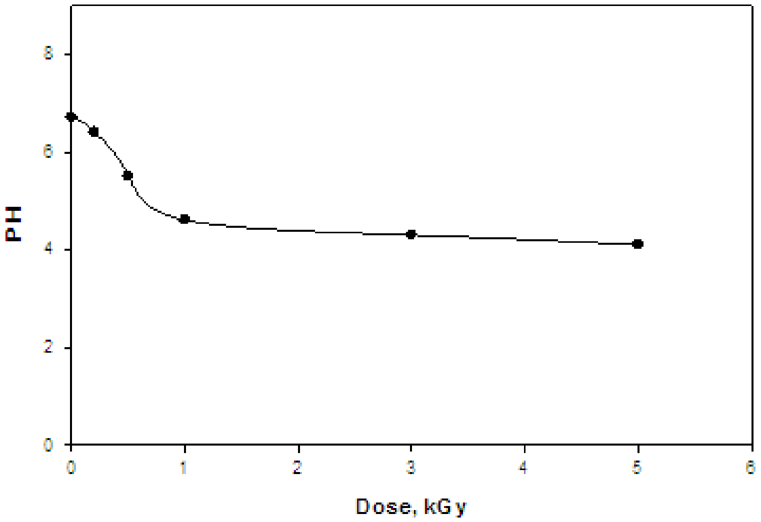


Fig. 10. Relation between change in pH of TBPE and absorbed dose.

Over view on both techniques used

The effective dose range exceeds in second technique due to avoid exposure of dye to gamma radiation, (significant effect of gamma radiation-non selective radiation-on TBPE dye participate in its degradation). Also, it is obvious that the slope of both curves (in direct technique and indirect technique) is significance different.

Conclusion

This approach for new radiation sensitive indicators by titrating acid-sensitive dyes with irradiated chloral hydrate may be useful. The solution can be used qualitatively as routine indicators in the range of 0.5-2.2kGy. Extend the applicable dose range to 5kGy is possible if avoid exposure of dye to direct gamma irradiation and proceed back titration with irradiated chloral hydrate.

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امكانيه استخدام مادة التيترابروموفينول فيثالين إيثيل أستر كمقياس للجرعات الأشعاعية في صورة سائلة

عبدالجواد محمد ربيع ، و عصام محمد فهيم* ، و شادية عبد المنعم* ، و محمود عبدالواحد الأهدل*

قسم الكيمياء ، كلية العلوم ، جامعة عين شمس ، و *قسم الوقاية و الجرعات الإشعاعية ، المركز القومى لبحوث و تكنولوجيا الإشعاع ، هيئة الطاقة الذرية المصرية ، ص. ب. ٢٩ مدينة نصر ، مصر.

دراسة المحلول المائي لمادة "التترابروموفينول إيثيل استر" (كاشف درجة حموضة) تحتوي على مادة "كلورال الهيدرات" بغرض الاستخدام كمقياس للجرعات الإشعاعية في الصورة السائلة و قد لوحظ أن مدى الجرعة الذي يغطيها هذا المقياس تمتد من ٠ر٥ الى ٢ كيلوجراي.

و بدراسة ثباتية المحلول لوحظ قدرة ممتازة على الثباتية قبل و بعد التشعيع في ظروف التخزين المختلفة ، و بمقارنة الطريقة المباشرة في تشعيع مادة "التترابروموفينول إيثيل استر" و الطريقة الغير مباشرة لتجنب تشعيع المادة لوحظ زيادة مدى الجرعة الإشعاعية الممتصة من ٢ الى ٥ كيلوجراي في الطريقة الغير مباشرة مما يلقى الضوء على مزايا استخدام الطريقة الثانية في القياس في مجال المحاليل المحتوية على صبغات حمضية أو قلوية.