SIMPLE OPTICAL READOUT FOR ETHANOL-CHLOROBENZENE DOSIMETRY SYSTEM

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Abstract

Optical readout of the ethanol-chlorobenzene (ECB) or Dvornik dosimetry system is based on the development of the coloured secondary complex of ferric thiocyanate which has a maximum absorption at 485 nm. The applicability of a rugged, hand-held, battery powered filter colorimeter operating at 480 nm has been investigated as a reader for this purpose. This simple reader performs very well within absorbance one displaying an excellent linearity of absorbance with the concentration of Cl^- ions. It is shown that by choosing the appropriate dilution factor when preparing the secondary complex solution the entire useful dose range of the dosimeter up to 2 MGy can be covered. The applicability of this reader to some other liquid chemical dosimeters is also discussed.

1. INTRODUCTION

The use of ethanolic solutions of chlorobenzene (CB) in high-dose dosimetry (ECB or Dvornik dosimeter) is based on radiolytic dechlorination of chlorobenzene and subsequent determination of hydrochloric acid formed in the irradiated solutions. The radiation-chemical yield of HCl, G(HCl), is a function of CB concentration, but at any constant CB concentration the value of G(HCl) is reproducible and independent of dose [1], dose rate [2] and incident radiation energy [3] over a wide range of these variables of interest in kGy/MGy dosimetry.

The ECB dosimetry system exhibits favorable metrologic properties with respect to both of its two fundamental aspects, radiation-chemical and analytical one. On the one hand, the radiation-chemical mechanism of the system's response to irradiation is sufficiently well understood [4], and has been characterized with respect to a number of variables, such as radiation quality [5], temperature of irradiation [6], etc. On the other hand, the ease of analytical determination of HCl in ethanol, and the availability of many analytical methods suitable for its quantitation [7] make it possible to choose a readout method for which the necessary equipment and/or sufficient experience already exist at the user's site.

Spectrophotometry has been known as one of the most versatile and sensitive analytical methods, and as such, one of the readout methods well suited for chemical dosimetry. Its application to ECB dosimetry involves the precipitation of insoluble $HgCl_2$ in the reaction between radiolytically formed Cl^- ions and the reagent Hg $(SCN)_2$, and subsequent complexation of the equivalent amount of liberated SCN^- ions with ferric ions. The ensuing red colored complex has a maximum absorption at 485 nm [8].

While spectrophotometry has not been suitable for field use until recently, recent advances in photonics, together with environmental needs and concerns have brought about a new generation of compact, hand-held filter colorimeters which could also be used as dosimetry readers.

This paper describes the use of a rugged, battery powered, hand-held filter colorimeter, operating at 480 nm, as an ECB dosimetry reader. Its performance has been checked against a Cary 2200 spectrophotometer and satisfactory characteristics have been established. The paper gives information necessary for the routine use of this reader in dosimetry practice.

2. EXPERIMENTAL

Absolute ethanol (Merck, *pro analysi*) and triply distilled water were mixed to prepare 96 vol% ethanol. It was then used for topping appropriate amounts of chlorobenzene (Fluka, *puriss.*) in volumetric flasks to obtain dosimetric solutions containing 4, 10, 20, 25 and 40 vol% of CB. The use of several formulations of dosimetric solutions is recommended for cross-checking of the internal consistency of measurements. The five formulations have been extensively used in the past and their characteristics are well known.

Commercial pharmaceutical ampoules (15 mm outer diameter) were filled with 5 mL of dosimetric solution. ECB solutions were partly deoxygenated by bubbling with nitrogen for 1 minute at about 30 mL/min immediately before flame sealing. Sealed dosimeters were stored in dark.

Dosimeters were irradiated with ^{60}Co gamma rays up to 25 kGy at dose rate of about 5 Gy/s. Irradiated dosimeters were opened and 0.1 mL of each dosimetric solution was transferred to 10 mL volumetric flasks. The reagent for developing color of the secondary complex was added to each volumetric flask and the flask was topped with technical grade 96% ethanol. The reagent consisted of 0.6 mL 5.25 mol/dm^3 $HClO_4$, 0.02 mL 0.37 mol/dm^3 $Fe(NO_3)_3$ and 0.2 mL saturated ethanolic solution of $Hg(SCN)_2$. At the same time, one blank of each dosimetric formulation was prepared in the same manner, using 0.1 mL of unirradiated dosimetric solution.

After completion of the complexation reaction and development of the colour, which takes less than half an hour, the coloured solution was divided in two parts. About 3 mL were filled into a 1-cm pathlength spectrophotometric cell, and the remaining 7 mL into a cylindrical 1-inch (25 mm) diameter borosilicate glass cell with screw cap.

The spectra of the secondary complex solutions between 750 and 300 nm were taken against the corresponding blanks with a Cary 2200 UV-VIS spectrophotometer by Varian, and absorbance at the maximum wavelength 485 nm was recorded. The colorimeter was a DR/700 model of a portable, digital, optical filter colorimeter by Hach. It uses plug-in filter modules with preprogrammed calibrations for various measurements. We used it in the absorbance mode with the 480 nm plug-in filter module and zeroed it with the appropriate blank solution.

The concentration of radiolytically formed HCl in irradiated dosimetric solutions was also determined by mercurimetric titration of Cl^- with $Hg(NO_3)_2$ in nitric acid-acidified ethanol, with diphenylcarbazone as indicator. The concentration of $Hg(NO_3)_2$ solution was checked daily by titrating standard solutions of NaCl.

3. RESULTS

One of the basic requirements expected of a chemical dosimetry system is the linearity of its response with dose. This requirement implies that the linearities of both of the two basic aspects of a chemical dosimetry system, radiation-chemical and analytical-chemical, should be fulfilled: the linearity of the radiation-chemical yield with dose, and the linearity of the response of the used analytical technique with the concentration of the analyzed radiation-chemical product.

The linearity of the radiation-chemical yield of the ethanol-chlorobenzene dosimetry system was the subject of several earlier papers [2, 7, 9]. The linearity of the spectrophotometric readout method was also established earlier [8]. The present work concerns itself with the suitability of a filter colorimeter as a readout instrument.

The results of colorimetric as well as of spectrophotometric readings of irradiated dosimeters are presented in the form of absorbance as function of irradiation dose to water for two extreme formulations of the ECB dosimeter, 4 vol% CB and 40 vol% CB in Figs 1a and 1b. While a good linearity of the spectrophotometric response of the 4 vol% CB formulation throughout the used dose range is obtained, the colorimetric response of the same formulation deviates from the linearity above absorbance larger than one. Admittedly, the spectrophotometric response of this formulation shows a tendency of sublinearity too at 25 kGy, which may be due to the consumption of about 2% of CB at this dose, and consequent decrease of the G(HCl) value. To compensate for all non-optical effects, the ratio of the absorbances taken by the two instruments was calculated relative to spectrophotometer and shown in the same figure as function of the spectrophotometer reading. Any nonlinearity of optical origin is enhanced in this ratio, and indeed, the sublinearity is seen to set in above absorbance 1 of the colorimeter.

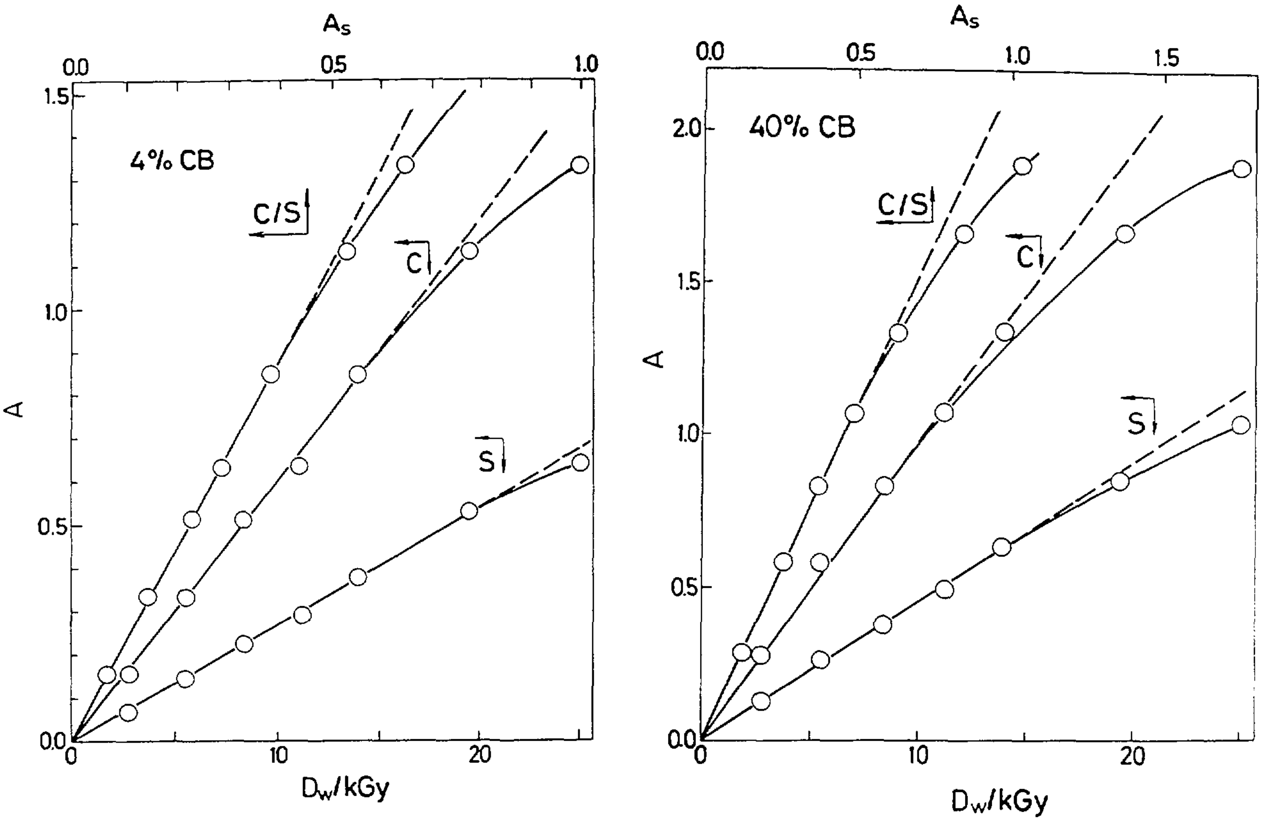

FIG. 1. Absorbance A as function of dose to water D_w as measured by a spectrophotometer (S) and a colorimeter (C). The dependence of the colorimetric absorbance on the spectrophotometrically obtained absorbance A_S is also shown (C/S). a) Formulation containing 4 vol% CB; b) formulation containing 40 vol% CB.

The same is seen in the formulation containing 40 vol% CB, and it may be reasonably assumed that this is a general phenomenon, and that it occurs at all intermediate CB formulations as well. It may also be concluded that it is not due to the decrease of the radiation chemical yield caused by the radiolytic depletion of the CB concentration, because this decrease would not amount to more than 0.3% at 25 kGy in 40 vol% CB formulation, which would have a negligible effect on $G(Cl^-)$.

Possible interference of the radiation-chemical aspect with the analytical-chemical one has been eliminated in the way Fig. 2 is presented. The absorbance scale is expanded and shown as function of the concentration of Cl^- ions independently quantitated by mercurimetric titration. A very good linearity of both, spectrophotometric and colorimetric responses is achieved within absorbance one in all formulations of the dosimetry system.

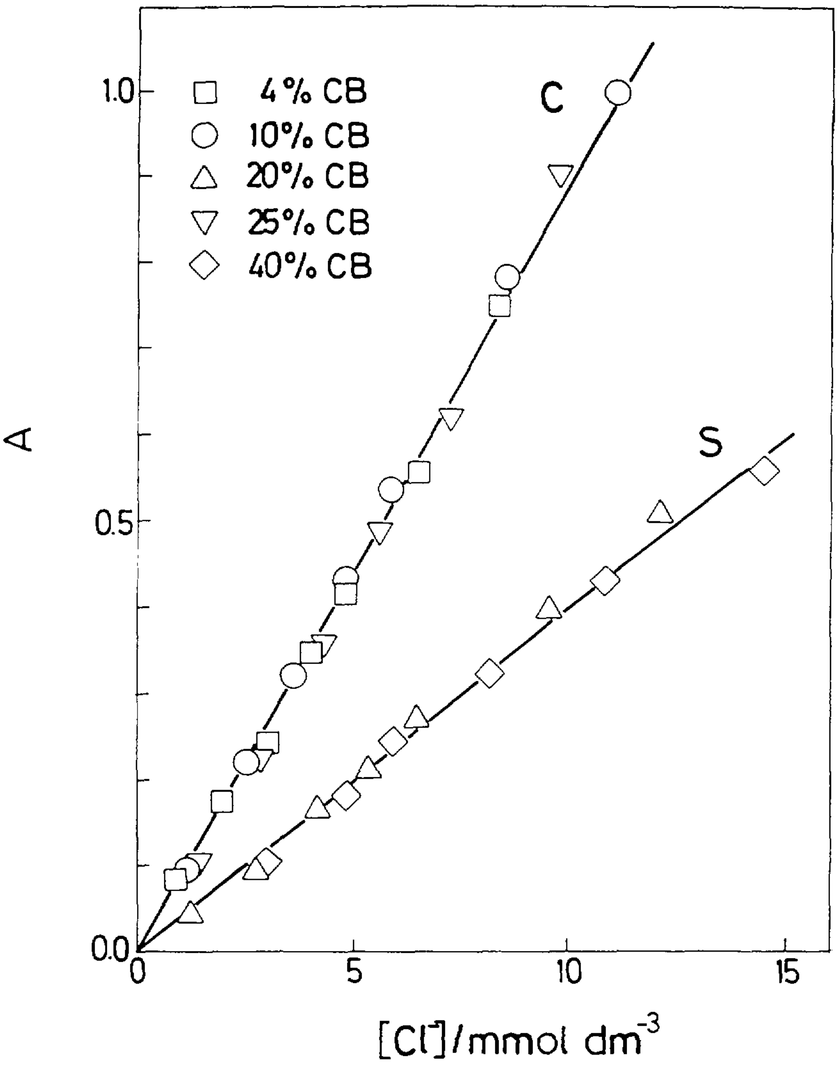

FIG. 2. Absorbance A as function of the concentration of radiolytically formed Cl^- ions as determined by a spectrophotometer (S) or a colorimeter (C) for various formulations of the ECB dosimeter.

Molar absorptivity ε of the ferric thiocyanate complex was calculated from the spectrophotometric data for each dosimeter formulation separately. No influence of the composition on ε was found, and the average value was 3800 ± 300 $dm^3mol^{-1}cm^{-1}$, which is 5% lower than the previously determined value (3990 $dm^3mol^{-1}cm^{-1}$) [8]. The conformity of the colorimetric readings to the Lambert-Beer Law permitted the effective pathlength of the cylindrical colorimetric cell to be calculated. The value 2.22 ± 0.07 cm was obtained as a ratio of the colorimetric and spectrophotometric absorbance at the same dose.

The validity of the Lambert-Beer Law of the colorimetric readout (the linearity) was examined beyond absorbance 1 by comparing the colorimetric and spectrophotometric readings up to the absorbance 2, the upper limit of the declared colorimetric range (Fig. 3). Above absorbance 1.5 the linearity rapidly deteriorates and the range above 1.3 is not recommended for dosimetry use.

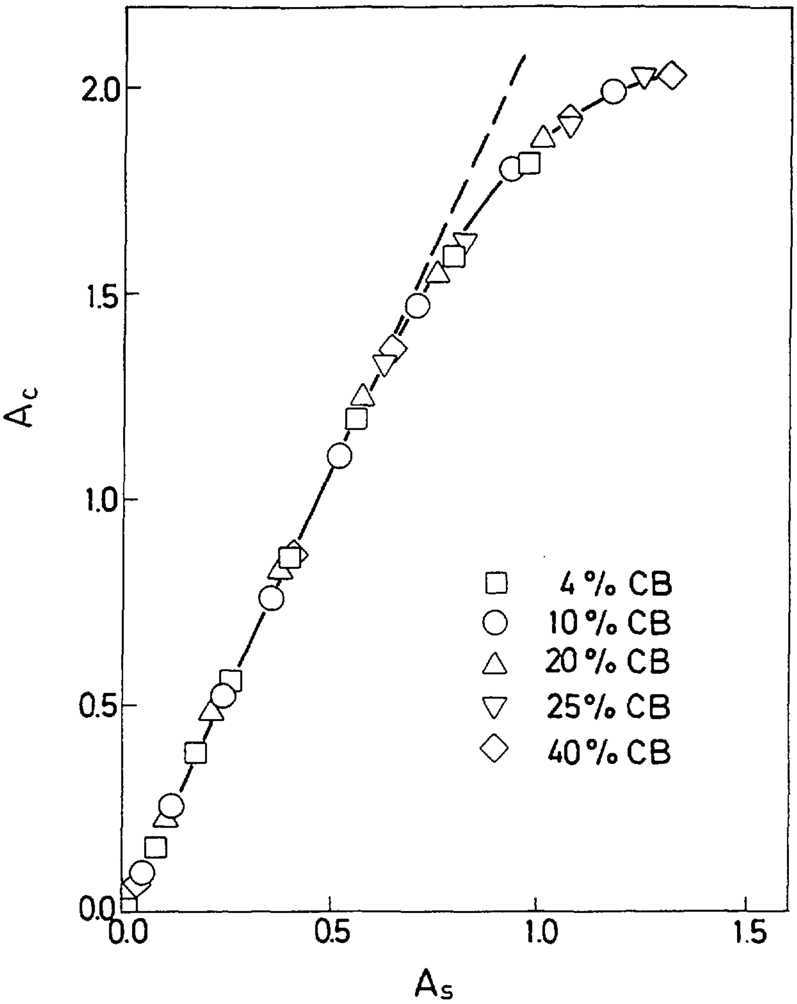

FIG. 3. Colorimetrically obtained absorbance A_C as function of the spectrophotometrically obtained absorbance A_S for the five formulations of the ECB dosimeter.

4. DISCUSSION

A great variety of physico-chemical changes inducible by irradiation, as well as a number of analytical methods available for their quantitation has led to a popular belief that almost anything can be a dosimeter. Potential new dosimetry systems are being investigated in hope that a special set of characteristics will be discovered, which might prove uniquely suitable for a particular purpose. At the same time, the scope of the well known dosimetry systems is improved by calibrating their response to an ever widening set of operating variables and applying novel readout techniques. However, technical and operational selection criteria impose restrictions upon prospective dosimetry systems, reducing the number of really useful chemical dosimeters to not more than a dozen.

It is not realistic to expect that the practicality of the use of the ECB dosimetry system could be enhanced by any modifications of the radiation-chemical aspect of the system's response to irradiation. A more productive approach to the improvement of the system's practicality would concern itself with the analytical-chemical (readout) aspects.

The oscillometric readout method of ECB dosimeters was one such improvement, which has greatly increased the practicality of the dosimetry system and has significantly contributed to its acceptance worldwide [10]. A simple optical readout method might be competitive in that respect, provided the limitations of a rugged filter colorimeter are recognized and taken into consideration.

The exponential law of light absorption is valid for monochromatic light. The optical filters used in the colorimeter have a typical bandwidth (Full Width at Half Maximum - FWHM) of 10±2 nm. The light source used in the colorimeter is focused by a bulb top lens, which cannot be considered a high-precision optics. Likewise, the silicon photodiode, unlike a narrow monochromator slit in a spectrophotometer, has finite dimensions and "sees" not only the light rays which arrive perpendicularly to it across the diameter of a cylindrical cell, but also the rays traversing distances somewhat shorter than the diameter. The light striking the front and the back surfaces of the cell is partly reflected from a cylindrical surface and does not reach the detector. All these optical imperfections cause nonlinear response of the instrument, but it is remarkable that this nonlinearity becomes evident only above absorbance greater than one. This leaves sufficient space for a quite satisfactory operation.

Spectrophotometric readout of the ECB dosimetry system depends on developing the colour of the secondary complex of ferric thiocyanate. The lower limit of the dose range is given by the smallest applicable dilution factor f when adding the reagents for developing the colour. Let us assume that the smallest achievable dilution of a 5-mL dosimetric solution involves taking 4.55 mL of irradiated dosimetric solution, adding 0.3 mL of $HClO_4$, 0.01 mL of $Fe(NO_3)_3$ and 0.1 mL of Hg $(SCN)_2$ solutions, and topping it to 5 mL with a few drops of ethanol. This gives the dilution factor 5/4.55=1.10. Let us further assume that the lowest reliable reading of the colorimeter is 3σ larger than the lowest possible reading, 0.01 absorbance units. This determines the lowest dose readings as given in Table I.

TABLE I. THE PARAMETERS OF THE COLORIMETRIC READOUT OF THE ETHANOL-CHLOROBENZENE DOSIMETRY SYSTEM

Formulation [vol% CB]	ε [$dm^3mol^{-1}cm^{-1}$]	ρ [kg/dm^3]	G [µmol/J]	Lower dose limit ($A\geq0.03$, f=1.10) [Gy]	Upper dose limit ($A\leq1.0$, $f=10^3$) [MGy]
4	3800	0.819	0.42	11.5	0.35
10	3800	0.839	0.52	9.1	0.27
20	3800	0.869	0.59	7.7	0.23
25	3800	0.880	0.60	7.5	0.23
40	3800	0.925	0.63	6.8	0.21

The upper dose limit is determined by the requirement that the absorbance should not exceed one, by the selection of a reasonable dilution factor, and by the operational upper limit of the dosimetry system. Giving weight to the last criterion, the operational upper limit is determined by the highest dose for which the response is known. This is beyond the linearity range of the response with dose, and amounts to about 2 MGy [1]. This in turn determines the dilution factor of 10^3, which is a reasonable value (0.1 mL of irradiated dosimetric solution diluted to 100 mL, or 0.01 mL diluted to 10 mL). Thus calculated theoretical upper limits (Table I.) may be even slightly larger than actually determined ones. In any case, the applicability of the colorimetric reader is demonstrated throughout the useful range of the ECB dosimetry system, while staying at the same time within the linearity range of the response of the instrument itself.

Let us briefly examine the applicability of the described colorimetric reader to other chemical dosimetry systems adopted as American Society for Testing and Materials (ASTM) standards [11] which are based on spectrophotometric readout. They are listed in Table II.

TABLE II. THE PARAMETERS OF THE COLORIMETRIC READOUT OF SEVERAL LIQUID CHEMICAL DOSIMETRY SYSTEMS

ASTM designation	Formulation	λ_{max} [nm]	Available filter module [nm]	G [µmol/J]	Dose range [kGy]
1026	1 mM $FeSO_4$ + 1 mM NaCl in 0.4 M H_2SO_4	304	not available	1.62	0.02 - 0.2
1025	15 mM$Ce(SO_4)_2$ + 15 mM$Ce_2(SO_4)_3$ in 0.4 M H_2SO_4	320	not available	0.231	0.5 - 5
	0.1 M$Ce(SO_4)_2$ + 0.1 M$Ce_2(SO_4)_3$ in 0.4 M H_2SO_4			1.066	5 - 40
1401	0.5 mM $Ag_2Cr_2O_7$ in 0.1 M $HClO_4$	350	not available	0.17	0.2 - 2
	0.5 m M $Ag_2Cr_2O_7$ + 2 mM $K_2Cr_2O_7$ in 0.1 M $HClO_4$	440	450	0.0395	5 - 40
1540	5 mM HHEVC + 17 mM HAc in 2-MEtOH	599	610	0.025	0.01 - 1
	5 mM PRC + 51 mM HAc in 2-MEtOH	549	550	0.033	0.01 - 3
	0.1 mM NFC + 17 mM HAc in DMSO	554	550	0.0031	0.1 - 30
	5 mM PRC + 17 mM HAC + 30 mM Ph NO_2 in DMSO	554	550	0.0040	0.003 - 40
	2 mM HHEVC + 34 mM HAc + 500 ppm Ph NO_2 + + 10% PVB in 85% (v/v) n-PrOH + 15 % (v/v) TEP	605	610	0.0051	0.05 - 5
	2 mM NFC+ 68 mM HAc + 500 ppm O_2N Ph COOH + + 10% (w/w) PVB in 85% (v/v) TEP + 15% (v/v) DMSO	557	550	0.0055	0.1 - 10
	100 mM HHEVC + 68 mM HAc + 500 ppm O_2N Ph COOH + 10% (w/w) PVB in 85% (v/v) TEP + 15% (v/v) DMSO	608	610	0.28	0.005 - 0.1

HHEVC - hexa(hydroxyethyl) pararosaniline cyanide
PRC - pararosaniline cyanide
NFC - new fuchsin cyanide
HAc - acetic acid
2-MEtOH - 2-methoxyethanol
DMSO - dimethyl sulfoxide
PVB - polyvinyl butyral
TEP - triethylphosphate

Contrary to the ECB system, which requires the developing of the coloured secondary complexes prior to readout, these other dosimetry systems exhibit an inherent change of optical absorption on irradiation. This means that no additional handling of the irradiated dosimeters would be necessary, and that they would, in principle, be ready for readout after the irradiation. Of course, the effect of irradiation on the glass of the container could be a problem interfering with the reading, and might require transfering the irradiated dosimetric solutions to transparent colorimetric cells. The difference between the absorption maximum and the readout wavelength of the plug-in module must also be checked, expecially if larger than 5 nm.

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