DEVELOPMENT OF FLUORESCENT, OSCILLOMETRIC AND PHOTOMETRIC METHODS TO DETERMINE ABSORBED DOSE IN IRRADIATED FRUITS AND NUTS

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Abstract. To ensure suitable quality control at food irradiation technologies and for quarantine authorities simple routine dosimetry methods are needed for absorbed dose control. Taking into account the requirements at quarantine locations these methods would require nondestructive analysis for repeated measurements. Different dosimetry systems with different analytical evaluation methods have been tested and/or developed for absorbed dose measurements in the dose range of 0.1–10 kGy. In order to use the well accepted ethanolmonochlorobenzene dosimeter solution and the recently developed aqueous alanine solution in small volume sealed vials a new portable, digital, and programmable oscillometric reader was developed. To make use of the availability of the very sensitive fluorimetric evaluation method, liquid and solid inorganic and organic dosimetry systems were developed for dose control using a new routine, portable, and computer controlled fluorimeter. Absorption or transmission photometric methods were also applied for dose measurements of solid or liquid phase dosimeter systems containing radiochromic dye agents, which change colour upon irradiation.

1. INTRODUCTION

The worldwide trade of agricultural products has shown continuous growth in the past decades and this tendency is increasing. Consequently the worldwide hygienic control of imported foods is of basic significance and requires high quality standardized control methods. Fresh and dried fruits, nuts, herbs and grains are often infested with insects, thus quarantine treatment is necessary for disinfestation. As the importance of fumigation as the most often applied method for insect control decreases significantly, the application of ionizing radiation has got new prospects recently. The correct use of radiation processing technologies requires correct dosimetry control methods, e.g. for dose distribution determination within the product packages controlling both the required minimum dose and the acceptable maximum dose. Quarantine authorities, on the other hand, often need simple routine methods to determine dose absorbed by the product on spot. The use of semiquantitative label dose indicators or simple, quick, easy to evaluate routine dosimeters with nondestructive analysis have got importance recently with respect to the increasing need of satisfying the regulatory inspectors at the importing stations to determine whether or not the irradiation for quarantine treatment was carried out correctly.

Fluorimetric, oscillometric and certain photometric methods possess the required simple and quick routine analysis applicable for dose determination.

2. EXPERIMENTAL

2.1. Chemicals and dosimeters

In order to determine absorbed dose applied during the gamma irradiation of the oscillometric, fluorimetric and photometric samples, ethanolmonochlorobenzene (ECB)

dosimeter solution was prepared and used as described elsewhere (1). The calibration procedure was carried out using the regularly applied 2 cm^3 nominal volume glass ampoules and traceability to national standards was assured. In the course of the present study a new 1 cm^3 nominal volume vial was also introduced and checked for routine use in the same, i.e. 0.4–100 kGy dose range.

A new polymeric thin wafer (0.5 mm thickness), containing a microcrystalline dispersion of a proprietary optically stimulated fluor in a plastic matrix has also been developed by Sunna Systems Corporation (2) and studied also by us for routine dosimetry using a simple, tabletop fluorimeter developed in Hungary.

βnaphthylamine, quinoline and naphthalene2carboxylic acid were of reagents grade and were used as received.

Tetrazolium violet, blue tetrazolium chloride, nitroblue tetrazolium chloride, tetrazolium red and phosphomolibdic acid from Fluka were also of reagent grade and used without further purification.

Solid state scintillators containing organic fluors, such as 1phenyl3mesityl2pyrazoline, 3hydroxyflavone and 2(2hydroxyphenylbenzathiazole) were produced by Bicron Co. (USA).

2.2. Irradiation facilities

The liquid and solid dosimetry samples, studied with oscillometry, fluorimetry and photometry, were irradiated with different 60Co gamma irradiation facilities. Irradiations were carried out within the source cage in a calibrated position of the SLL01 type gamma source (3 PBq) of the Institute of Isotopes Co. Ltd. and with the Gammacell 220 type gamma irradiation facility (0.7 PBq) of the National Institute of Standards and Technology (Gaithersburg, USA).

The electron irradiations were carried out with the 4 MeV linear electron accelerator (LPR4 type, Tesla Vuvet, Praha, Czech Republic) of the Institute of Isotope and Surface Chemistry (Budapest, Hungary) using 2.6 μsec pulses, 25 cm scan width and 1 Hz scanning frequency.

2.3. Instrumentation

Oscillometric measurements were performed with the OK302/2 type oscillotitrator of Radelkis (Budapest, Hungary). The new 1 cm^3 volume ECB containing vials were tested with a new, digital oscillometric reader built recently by Sensolab Ltd. (Budapest, Hungary).

The fluorimetric investigations were carried out with the LS5 Luminescence Spectrometer (PerkinElmer), with the Clinifluor 88 PT routine fluorimeter (Institute of Isotopes Co. LTD) modified for our purposes and with the routine, programmable fluorimeter produced by Sensolab Ltd.

The spectrophotometric measurements were performed with the Jasco V550 UVVIS and the Cary 14 UVVIS spectrophotometers.

3. RESULTS AND DISCUSSION

3.1. Oscillometric investigations

Oscillometry is an electroanalytical method of conductivity measurements, where high frequency alternating current is applied to measure or follow changes in the composition of chemical systems. The ampoule containing the solution under test is placed either between the plates of a capacitor (capacitive cell) or inside the inductance coil (inductive cell) of an oscillator. The main advantage of the method is that the electrodes are not in direct contact with the solution, thus the analysis can be carried out in sealed ampoules too. Thus the method is nondestructive, making possible the quick, repeatable, routine dose evaluation of the irradiated dosimeters.

The ethanolmonochlorobenzene dosimeter solution is a well known reference and routine system for dose control in radiation processing in the 0.4–100 kGy dose range using oscillometric evaluation method (3). The original dosimeter system applies an analogue oscillotitrator for the evaluation of the irradiated solution. The nondestructive analysis makes possible the repeated evaluation of the irradiated dosimeters at any time after irradiation and according to our experiences irradiated ECB dosimeters can be evaluated in case of suitable storage 15 years after irradiation with a reproducibility of ±4%.

In order to carry out quick routine measurements for the present purpose i.e. at quarantine locations a new, portable, digital oscillometric reader was designed and built, suitable for measurement with both 2 cm^3 and 1 cm^3 nominal volume ampoules. Due to the necessity of using a small size dosimeter a new, 1cm^3 volume, sealed glass vial (diameter: 7.2 mm; wall thickness: 0.55 mm, produced by Chromacol, USA) was introduced to store the dosimeter solution. The new oscillometric reader, which can be connected to a PC, contains a builtin software making possible the calculation of absorbed dose by using the mathematical function of the calibration curve measured with the reader using ECB dosimeters calibrated previously. Since it was found earlier that the best fit was given by applying 3rd order polynomial this function is stored in the memory of the new reader.

The new system, i.e. the new reader and the 1 cm^3 vial, was tested with respect to routine application in the required dose range. The sealed vials were checked concerning their storage capabilities, i.e. the amount of liquid sealed in the vial was measured from time to time in order to test any leakage, but no change was observed after even 3 months storage. The diameter of the vial was also controlled and was found to vary between 6.9 mm and 7.4 mm. Thus, due to the diameter dependence of the oscillometric evaluation the vials must be selected and corrections have to be applied with respect to the calibration vials (7.1 mm ± 0.1 mm) similarly to the 2 cm^3 ampoules.

The vials were then irradiated in the 0.4–100 kGy dose range and measured with the new reader. The response of the system, i.e. the calibration curve is shown in Fig. 1. The results indicate, that the ECB solution can be used for dose evaluation with the new type oscillometric reader and applying the 1 cm^3 nominal volume vials in the same dose range as used with the previous analogue oscillometric system.

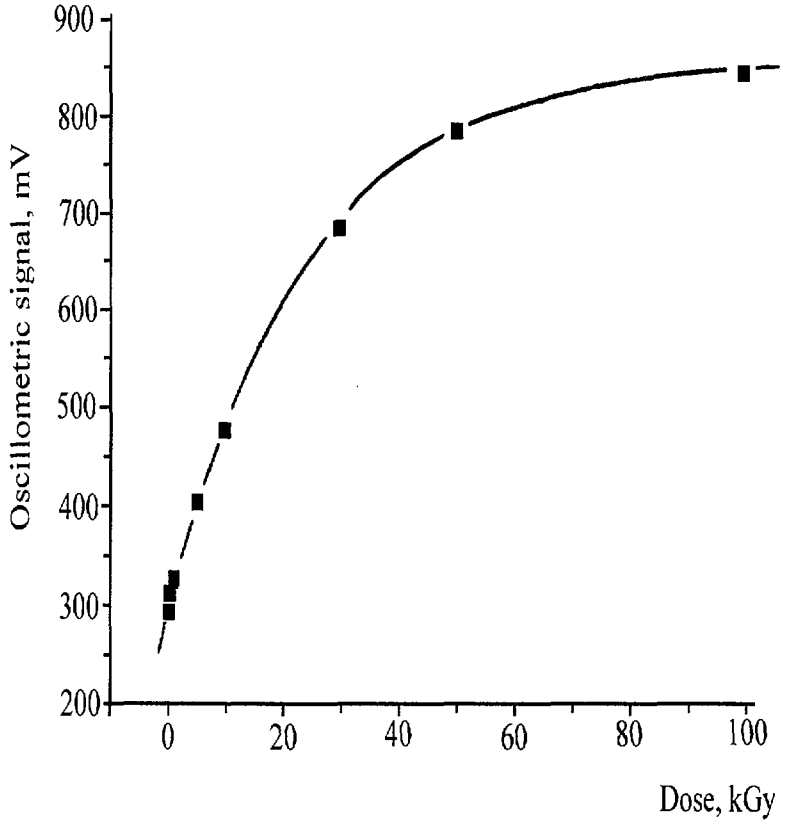

FIG. 1. Dose response of the oscillometric signal of ECB solution irradiated in 1 cm³ vials.

3.2. Fluorimetric investigations

Fluorimetry is a versatile method of dosimetry with the possibility of carriyng out measurements in a wide dose range. It is based on the measurement of OSL (optically stimulated luminescence), when a molecule — excited by UV or visible light — emits part of its energy in the form of light while returning to ground state. The intensity of the fluorescent light is related to the concentration of the fluorescent compound produced by radiation. In this case the original compound (i.e. the sample studied for possible use for dosimetry purposes) does not give fluorescence before irradiation, since the fluorescent compound is a radiation product [4].

It is also possible to study such a molecule, which originally contains a fluorescent compound (e.g. fluorescein or its derivative). This compound is then destroyed by radiation and the original intensity of the fluorescent light decreases. This decrease can again be the measure of absorbed dose.

In our investigations we have studied the possible use of some organic compounds like naphthalene1 and 2 carboxylic acids, βnaphthylamine, quinoline in aqueous solution as well as in solid matrix. By exciting the previously gamma irradiated basic aqueous solution of 20 mmol dm^3 naphthalene2carboxylic acid with 365 nm light a dose dependent emission was observed at 420 nm in the dose range of 0.1–100 kGy. In the case of gamma irradiated aqueous solutions of βnaphthylamine and quinoline precipitation was observed due to irradiation which became more and more significant with increasing dose. These compounds were then used in gelatin and polyvinylalcohol (PVA) and irradiated in the dose range of 0.1–50.0 kGy. The investigations concerning their applicability needs continuation.

Taking into account the simpler use of solid samples the possible use of originally fluorescent solid state plastic samples for dosimetry purposes was also investigated. Three different compounds, i.e. 1phenyl3mesityl2pyrazoline (PMP), 3hydroxyflavone (3HF) and 2 (2hydroxyphenyl) benzathiazole (HBT) in plastic matrix were irradiated in the dose range of 0.1–100 kGy and the excitation and emission spectra of the samples were measured. In the case of the PMP (excitation wavelength: 330 nm; emission wavelength: 425 nm) and 3HF (excitation wavelength: 355 nm; emission wavelength: 530 nm) (Fig. 2) the intensity of fluorescent light decreased with increasing dose, while in the case of HBT (excitation wavelength: 350 nm; emission wavelength: 517 nm) no significant change with respect to the fluorescent light intensity was observed. A simple routine fluorimeter (Clinifluor 88 PT produced by the Institute of Isotopes Ltd. Co., Budapest, Hungary) was found to be suitable for routine dose determination in the dose range studied.

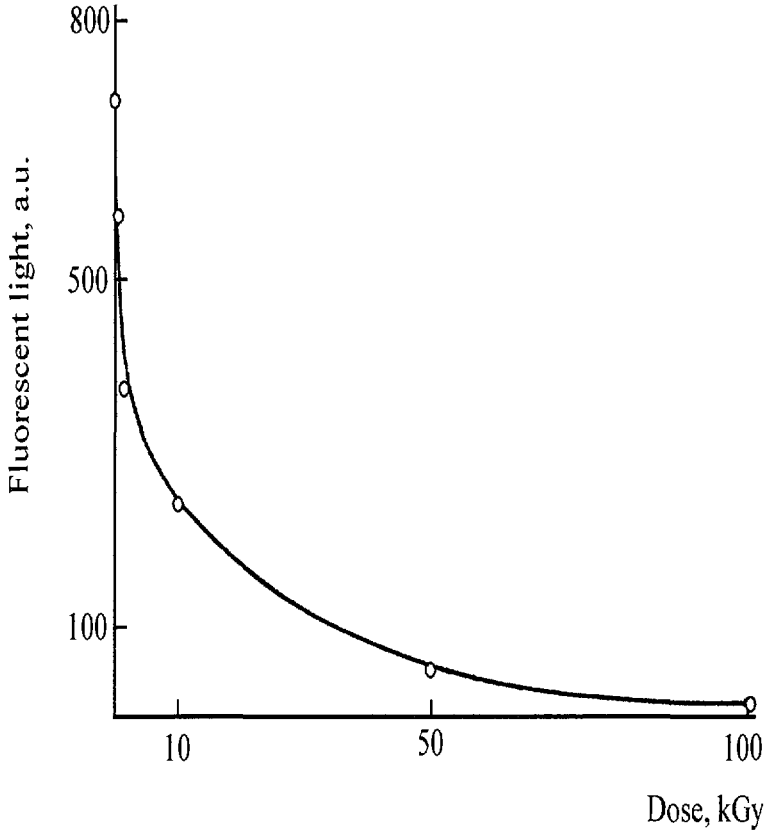

FIG. 2. Dose dependence of the fluorescent light originating from the BCF9950 fluor sample containing 3 hydroxyflavone.

Commercially available perspex (polymethylmetacrylate, PMMA) samples were irradiated in the dose range of 1–100 kGy and the fluorescent light intensity was measured at 480 nm (excitation wavelength: 350 nm). Since increasing fluorescent light intensity was observed with increasing dose it is assumed that a photofluorescent compound was produced upon irradiation. Due to the fact that various perspex samples are available commercially of different origin detailed investigations are needed with respect to stability and reproducibility when such samples are considered for dose measurements using fluorimetric method.

Optically stimulated luminescence dosimetry using inorganic microcrystalline solidstate fluors dispersed in a polymer matrix is a well known method for measuring low and high doses [2]. The potential applicability of a new film, the SUNNA dosimeter film, which contains an optically stimulated fluor in a plastic matrix, was also studied. The 0.25 mm thick film was irradiated in the 0.01–100 kGy dose range and the OSL signal was measured with a tabletop, routine fluorimeter exciting the irradiated 2.0 cm × 3.8 cm film samples at 450 nm. The emitted light was measured at 650 nm and 700 nm respectively. The response of the gammaray irradiated films was measured 1 h and 24 h after irradiation. There is a linear response up to about 40 kGy (Fig. 3), while at higher doses (30–100 kGy) significant sublinearity appears. This sublinearity, however, becomes nearly linear after 24 h storage. According to our investigations this OSL signal is not changed by many readout cycles and it is also not affected by light and humidity. The film has got a wide dynamic range, it is dose rate independent, is simple to use and is rugged. On the other hand it shows a slight temperature dependence and especially at high doses some instability for the first few hours after irradiation [2].

For routine measurements a programmable digital fluorimeter has been developed, which reads and evaluates the SUNNA film taking into account the calibration curve stored in its memory, but connecting it to a PC is also available.

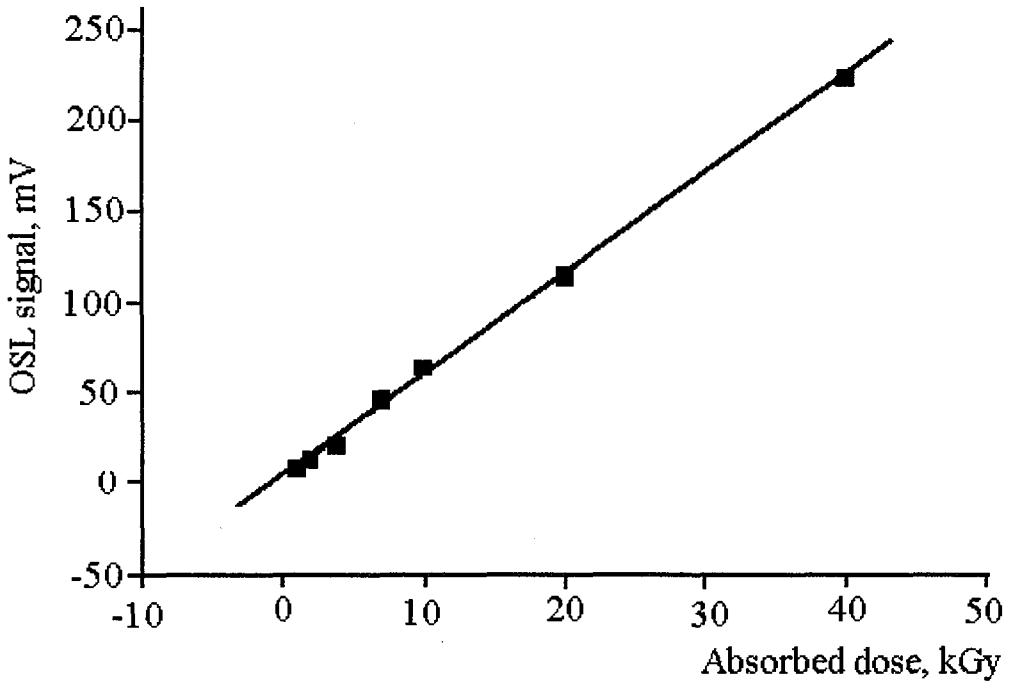

FIG. 3. Photofluorescent gammaray response of the 0.25 mm thick SUNNA dosimeter film measured one hour after irradiation at 650 nm.

3.3. Photometric investigations

Various types of radiochromic dye films are in regular use for absorbed dose measurements in radiation processing. The chemical background of these systems is the color change induced by radiation, i.e. the change from colorless to strongly colored takes place during irradiation and there is a relationship between this color change and the dose absorbed in the system. These radiochromic dye systems can be applied for dosimetry purposes both in liquid and solid state (films) [5].

Taking into account the request for developing a "label" system for dosimetry purposes different type of tetrazolium salts have been studied for potential application.

3.3.1. Nitroblue tetrazolium

Detailed investigations have been carried out to study the radiation chemical characteristics of this dye in order to determine the most suitable composition of the dye solution to be used in a solid host material. It was found that upon irradiation — due to a reductive process — highly coloured mono and/or diformazan radiolysis products form showing a dose and pH dependent absorption in the 500–600 nm region (Fig. 4). The formation of this product is much more pronounced at basic pH, i.e. at above pH ~10 and when the aqueous solution contains also approx. 0.1–0.5 mol dm^3 ethanol. In air saturated, aqueous solutions at basic pH together with the lilac colour of the irradiated solution precipitation takes place, while this precipitate gets dissolved in those solutions which contain e.g. ethanol.

Analyzing the results of the dose effect study our conclusion was, that aqueous solutions containing 1 mmol dm^3 dye can be used for dose measurements in the range of 0.01–1.0 kGy, where linear relationship between absorbance of the formazan formed (670 nm) and absorbed dose was found (Fig. 5).

3.3.2. Other tetrazolium salts

The potential use of aqueous solutions of blue tetrazolium chloride and tetrazolium violet was also studied for dosimetry application. The solutions containing 10 mmol dm^3 solute were irradiated in the dose range of 0.01–5.0 kGy and similar absorption spectra to the one observed in the case of nitroblue tetrazolium chloride were found indicating the same type of radiolysis product formation. These solutions are now under investigation concerning their potential use for dose determination in different concentrations, composition and pH.

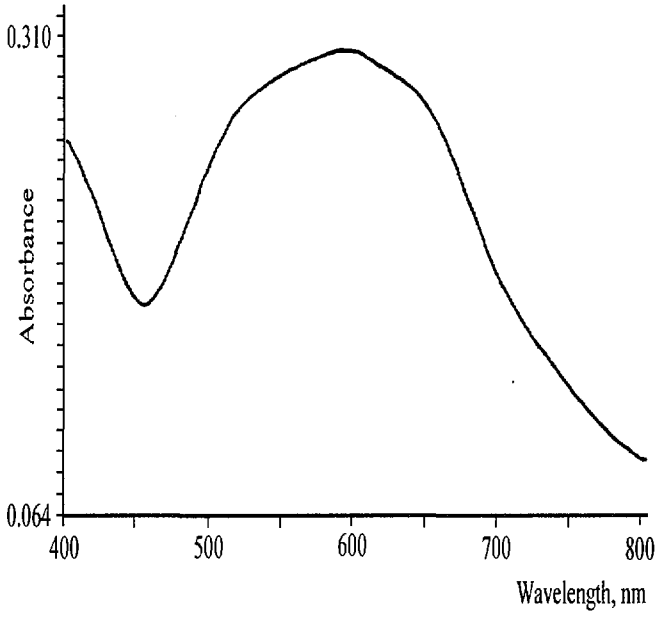

FIG. 4. Absorption spectrum of the irradiated nitroblue tetrazolium solution containing 0.5 mol dm^3. tertbutanol (pH = 10.3).

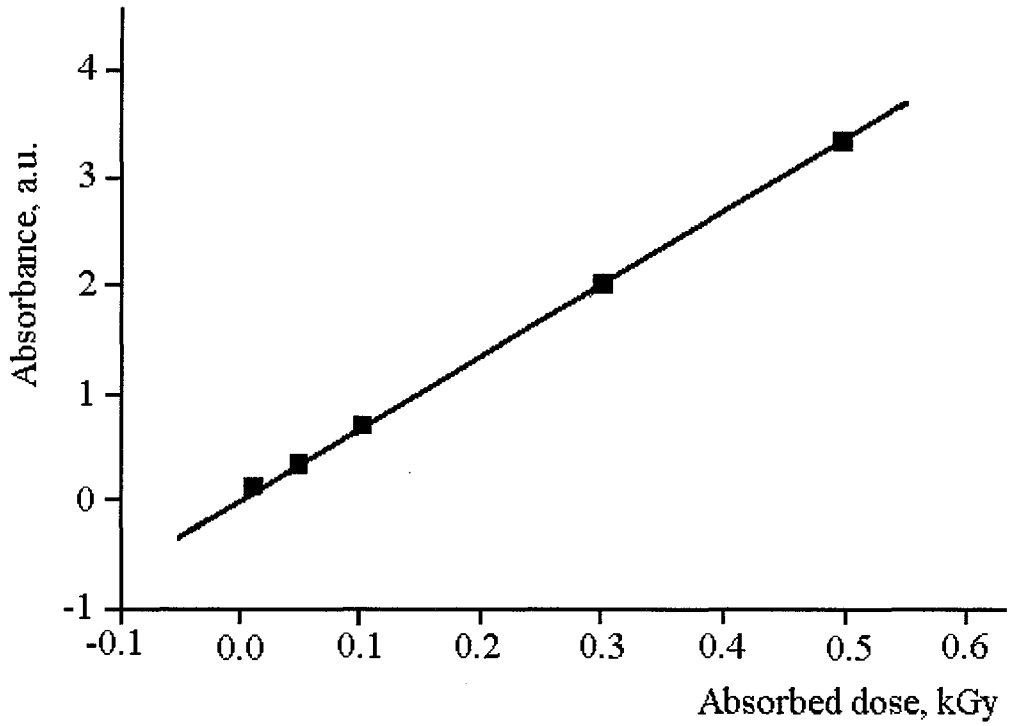

FIG. 5. Dose response of the absorbance (670 nm) of the irradiated aqueous nitroblue tetrazolium solution (pH = 11). (The overall uncertainty of the measurement at one standard deviation is estimated to be ±6%, as based on the statistical evaluations, i.e. type A uncertainties.)

3.3.3. Solid formulation of dye compounds

In order to develope solid phase label type systems both the fluorimetric and the photometric solutions studied so far were investigated with respect to their formulation in solid host materials. In the course of the first measurements gelatin and polyvinilalcohol (PVA) were used.

Aqueous solutions of quinoline and βnaphthilamin were mixed with gelatin and polyvinilalcohol (PVA) solutions respectively and the resulting dried samples were irradiated in the dose range of 0.1–50 kGy. The color gels formed upon irradiation are under detailed investigation for potential dose evaluation using both photometric and fluorimetric analysis.

Aqueous tetrazolium red solutions were also mixed with polyvinilalcohol solutions, dried and irradiated in the dose range of 0.1–10 kGy. The red colored gels formed upon irradiation are also studied for potential use as dose indicators and/or label dosimeters.

4. CONCLUSIONS

The oscillometric analysis of the ECB solution filled in the 1 cm^3 vials and analyzed with the new oscillometric reader gives more convenient application concerning nondestructive readout possibilities even in the low dose range from 0.4 kGy.

The application of the new SUNNA dosimeter film with OSL analysis provides convenient evaluation of as low as 10 Gy doses with repeated readout possibilities similarly to the oscillometric analysis. It is important to note that due to its size it offers good dose evaluation possibilities for electron beam applications too.

Tetrazolium salts both in aqueous solution and in gel and film form show promise for dose determination in the dose range of 0.01–10 kGy using both photometric and in certain cases fluorimetric evaluation method.

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