UNIVERSITY OF CAPE COAST

CHARACTERISTICS OF TETRAZOLIUM VIOLET FOR RADIATION PROCESSING DOSIMETRY

BY

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DECLARATION

Candidate's Declaration

I hereby declare that this dissertation is the result of my own original work and that no part of it has been presented for another degree in this university or elsewhere

Candidate's Signature. ………………………… Date…30 June 2008

Name: Geoffrey Emi-Reynolds

Supervisors' Declaration

We hereby declare that the preparation and presentation of the dissertation were supervised in accordance with the guidelines on supervision of dissertation laid down by the University of Cape Coast.

Principal Supervisor's Signature. John Justice Fletcher Date. 6 Aug, 2008

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ABSTRACT

The dosimetry characteristics of 2, 5-dipheny-3-(1-naphthyl)-2H-tetrazolinum Chloride (TV) for radiation processing has been investigated for gamma and electron beam irradiation processing.

The steady state investigations of the TV solutions were undertaken using the panoramic facilities of the Institute of Isotopes (Budapest, Hungary) and the Radiation Technology Centre of the Ghana Atomic Energy Commission in Ghana. The dynamic studies were carried out using the 4 MeV LPR- type linear Accelerator of the Institute of Isotopes (Budapest, Hungary). In all cases U-V spectrophotometers were used to establish the absorbed dose by measuring the absorbance of the film or solution with the peaks occurring in the 500-600 nm range.

The investigations included the effect of solute concentration and solvents used on the performance of both the solution and films systems, the effect of pH, irradiation temperature, humidity and the stability of the dosimeter system both as solutions and is in radiochromic dye films.

The observations made indicate that the TV undergoes a-two electron reduction process as in other reported cases to form the violet coloured formazan, the extent of colour change being dependent on the dose, the concentration and the pH among others. The 1mM-TV solutions for instance may measure doses up to 50 kGy and a radiochromic dye film prepared from it may go up to 60 kGy. If N_2 saturated, the solutions may be used for low dose irradiation below 1kGy and the addition of alcohol also improvise the low absorbed dose measurements. The prepared solutions and films are generally stable if stored in the dark but temperature during and after irradiation affects the readout. The

temperature effect therefore requires that in all cases in-plant calibration of the system be carried out. Again it has been established that increased relative humidity increases the absorbance of the film for the same given dose, which also requires that the films must be conditioned at all times to ensure reproducible results.

Finally preliminary tests carried out both in industrial gamma- and electron beam facilities have shown promise for the routine use of this dosimeter system both as a solution and as a film.

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DEDICATION

TO MY WIFE

MRS REBECCA EMI-REYNOLDS

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CHAPTER 1

INTRODUCTION

Introduction

The potential value of ionising radiation was recognised soon after the discovery of X-rays in 1895 (Röntgen, 1896) and radioactivity in 1896 (Becquerel, 1896). Since then attempts have been made to apply this discovery to develop applications for the benefit of all mankind taking advantage of the peculiar properties of ionising radiation.

The first use of ionising radiation was in medicine where the penetrating properties of X-rays were utilised for diagnosis. In the meantime the basic studies of (Lind, 1912), using radium and its decay products and applied research (Coolidge, 1913) using an electron beam accelerator, blazed the path that, years later after the World War II, led to the development of almost all of the known industrial applications of ionising radiation. The lack of suitable radiation sources to support a viable radiation processing industry delayed the commercial application of the technology until the discovery of the nuclear fission of uranium in 1939. The subsequent rapid development of nuclear reactors in the post war period led to the production of intense radionuclide sources of penetrating γ rays for treatment of large volumes of material to high radiation doses.

By 1958 the early expectations of a commercial use of ionising radiation for the benefit of mankind began to turn into reality. A number of promising radiation applications were under investigations (U. S. Atomic Energy Commission, 1959;

Brownell, 1961; and at least two of these; the radiation sterilization of medical supplies and radiation induced cross-linking of polymers were in commercial operation in the United States of America. A new industrial technology, where large doses of radiation are used to induce specific biological, chemical or physical effects to obtain new commercial products with better properties than the ones obtained with conventional methods, was going to develop. Since then the radiation processing industry has prospered and continues to expand. At present the world total sales of irradiated products is estimated at several billions of dollars per year, and it continues to grow at a rate of 10 – 15 % per year (Bradley, 1986). Indeed it is likely that people everywhere in the world come into contact with radiation processed goods every day without being aware of it.

The vehicles, on which we move around, be they cars, buses, planes or trains have parts or components that are radiation-processed materials: the paint of the dashboard may have been cured by electron beam, while there is a fair chance that the tyres contain irradiated rubber. Much of the foamed plastics used as electrical, thermal or noise insulating materials might well be irradiated plastics. Ion-exchange membranes, used as separators and made by a radiation grafting method can be found in tiny alkaline batteries. Packaging materials and wrapping films for food products, electrical wires and cables and water pipes are other common examples of irradiated materials. One may encounter other radiation-processed products at the doctor, or dentist or at the hospital.

The practical application of highly intense ionising radiation has therefore become more and more important in many areas like medicine, agriculture, environmental protection, industry, etc. The radiation sterilization of medical devices and pharmaceuticals as well as the modification of polymers using ionising radiation has got wide-spread application all over the world during the past three decades. The irradiation of different foods and agricultural products, the production of biomaterials and the introduction of environmentally friendly technologies to save nature and natural resources using ionising radiation are emerging technologies. There are about 250 high activity ^{60}Co gamma irradiation facilities and about 800 electron beam accelerators in operation both in highly developed and in developing countries worldwide.

The safe operation of these facilities and the suitable execution and achievements of the objectives of the radiation processing technologies require process control methods, which can guarantee the quality of the irradiated product. Radiation dosimetry has become the most reliable and independent method for process control. At present there are millions of dosimetry measurements carried out yearly, with stringent requirements concerning the applicability of the different dosimetry systems. The radiation sterilization, cross-linking of polymers and food irradiation technologies apply high doses in the kilogray (kGy) range. Other applications like sprout inhibition, mutation breeding activities and sterile insect techniques require much lower doses. Consequently the accurate determination of doses is of basic significance for controlling these technologies. Due to worldwide standardization procedures, the dosimetry methods applied for process control must fulfil strict requirements. The role and significance of dosimetry is increasing as it is also shown by the introduction of new International Organization for Standardization (ISO) and American Society for Testing and Materials (ASTM) dosimetry standards. Recently the ISO has resolved to adopt the ASTM radiation processing dosimetry standards into the ISO system to harmonise dosimetry procedures (ASTM Subcommittee E10.01 progress report, 1998).

There are several physical and chemical methods for the determination of absorbed dose and dose rate whose application are affected by various factors like dose, dose rate, temperature, humidity, energy of radiation among others. For this reason different dosimetry systems have different ranges of application, reproducibility, accuracy and environmental response characteristics. For instance, food irradiation has about three groups of dosimetry systems that apply. When processing against weevil infestation and for sprout inhibition doses are limited to below 1 kGy, whereas decontamination and processing against moulds may go up to 10 kGy or even 30 kGy for decontamination of some foods especially for patients whose immune system have broken down and for foods for astronauts. In the case of medical sterilisation, doses may go up to 50 kGy or higher, while in the modification of industrial materials, as high as 500 kGy may be required. The application or processing requirement of a product therefore plays a very important role in the selection of the dosimetry system suitable at a given instance. Therefore the choice of a suitable dosimeter system for a given task requires the consideration of many factors which must be known for the dosimeter system.

Primarily, there are two main dosimetry systems which are used in radiation processing technologies and which may be classified as liquid or solid state systems. The liquid systems are available to measure the integral dose across the volume of the ampoules or containers which carries the liquid. Examples of liquid systems include the Fricke or ferrous ammonium sulphate system, ceric-cerous system, ethanol chlorobenzene system and dichromate system among the main ones. They have different characteristics with respect to their use including the readout system, range of application, influence parameters, etc. except that they are all liquid and chemical systems. One disadvantage of these systems is the possibility of the ampoules getting broken during usage and the fact that by their size the measured dose is always with reference to a volume and not to a point. Being liquid systems, their densities are normally very close to the biological materials which are processed by radiation, thus eliminating the use of elaborate correction factors.

The plastics (Perspex systems) or film systems (i.e. radiochromic films – where a dye is contained in the material; coated films – Gafchromic – where there is a thin (7 μm) active layer coated on the surface of the matrix, also films of one component – CTA, where radiation induced products or bonds are measured are all solid systems). These doses are evaluated by measuring the absorbance using spectrophotometry. The Sunna system is a special type of film, where the optically stimulated luminescence is measured by fluorimetry. Generally films have characteristic properties which are altered on the absorption of radiation energy. They are suitable for measuring doses within small volumes or locations because of their relatively small size and evaluation techniques, i.e. scanned densitometry. They are mostly affected by environmental conditions like temperature and humidity, (i.e. during, before and after irradiation) and have to be used with care. Like the liquid systems their use are governed by their range of application and the influence parameters. There are a few (FWT-60, B3, CTA, Sunna) film systems in use for food irradiation, medical sterilization and for the treatment of industrial products depending on irradiation conditions and the accuracy and uncertainty permitted for the given product being processed. One such system which has recently been developed but which does not have a radiochromic material in it is the Sunna system. This system rather has a lithium fluoride powder (i.e. crystals) impregnation in polyethylene matrix and the dose is measured using fluorimetry (i.e. the excitation of the system is carried out with light instead of heat). Again the densities of these films are normally very close to the biological materials (tissue equivalent) which are processed by radiation thus avoiding the use of elaborate correction factors.

Other solid systems include powdered materials like the alanine, diodes and lithium fluoride for use in thermoluminescent dosimetry among others. Such dosimeters have different characteristics and use. Depending on the size and readout system, they may be used for dose rate measurement as with diodes, and may be used for food irradiation, medical sterilisation or for other industrial processing. They are less affected by environmental conditions like humidity and temperature.

All these groups of dosimetry systems may be divided into four classes according to their relative quality and areas of application, such as the primary standard, reference standard, transfer standard and routine dosimeters. The primary standard dosimeters (i.e. which do not require calibration) are established and maintained by national standards laboratories for calibration of radiation fields and other classes of dosimeters. The two commonly used primary standard dosimeters are ionisation chambers and calorimeters. Reference standard dosimeters are used to calibrate radiation fields and routine dosimeters. These dosimeters may also be used as routine dosimeters within their dose ranges. Transfer standard dosimeters are specially selected for transferring absorbed dose information from an accredited or national standards laboratory to an irradiation facility in order to establish traceability for that facility. These dosimeters are recommended to be carefully used under conditions that are specified by the issuing laboratory. Transfer standard dosimeters may be selected from either reference standard dosimeters or routine dosimeters taking into consideration the criteria necessary (i.e. taking note: of the necessary pre- and post irradiation stability, since evaluation take place long after irradiation) (ISO/ASTM Guide 51261, 2002). Routine dosimeters may be used for radiation process quality control, dose monitoring and dose mapping. Proper dosimetric techniques, including calibration are required to ensure that measurements are reliable and accurate. Examples of routine dosimeters, along with their ranges are given in the discussion of the individual dosimeters later under literature review.

In spite of the several dosimetry systems developed for dose control in radiation processing, only a few systems are suitable for reliable dosimetry measurements. This stems from the fact that the requirements are getting stricter and stricter, while there is a tendency to apply simpler and cheaper systems, particularly for new technological applications. All these conditions and claims point to the fact that the search for new dosimetry systems with unique characteristics as discussed above must proceed. Additionally the step by step spreading of the electron beam irradiation facilities also require suitable film dosimeters, and due to the more complex dose distribution mapping in irradiated products compared to the case in gamma irradiated products, dosimetry systems of high resolution are required. For these reasons the quest for new dosimetry systems are always being pursued by researchers across the world.

With the introduction of new dosimetry systems, more detailed investigations are needed to clarify all factors and potential environmental effects which can affect the performance and accuracy of these systems. The incomplete knowledge of these effects or the lack of the necessary corrections during dose determination procedures can lead to serious errors during calibration, operational qualification, product performance qualification and hence unreliable routine process control.

Objectives and scope of this study

The wide use of ionising radiation in industry, medicine, agriculture, environmental technology, i.e. radiation processing in general, is increasing world-wide resulting in the growing need for reliable quality control dosimetry methods. In accordance with the existing needs to satisfy these requirements and particularly in radiation processing dosimetry, the present work was embarked upon to study the characteristics of tetrazolium violet both in solution (i.e. liquid) and in the solid phase (i.e. film) through the measurement of colour-changes associated with it as a radiochromic dye system, upon irradiation.

Radiochromic effects mean the direct colouration of a compound or material exposed to ionising radiation resulting in permanent coloured images which are used for dose evaluation. During the past two decades various types of radiochromic dosimeters with different sensitivities have been developed by many researchers like McLaughlin et al., (1977), Janovsky et al., (1994), Kovacs et al., (1995) among others. At the same time new technologies have emerged, which require more and more specific dosimeter systems, hence the need to pursue the agenda of developing new dosimetry systems.

Tetrazolium salts have long been known as heterocyclic organic compounds (i.e. quaternary ammonium compounds) with a significant property of forming water insoluble, highly coloured formazans by reduction (Altman, 1976). Due to this characteristic property and their low reduction potentials these compounds have been used as reagents for the detection and study of reducing enzyme systems and for the detection and estimation of reducing functions of organic compounds (Altman, 1976). They have also been used in botany as colouring compounds sensitive to UV radiation, to estimate the viability of seeds of agricultural plants, to distinguish between normal and malignant tissues and as analytical reagents to detect O_2^- radical ions (Farber et al., 1956 and Altman, 1976).

The two-electron reduction process of tetrazolium salts was extensively studied by Pikaev and Kriminskaya, (1998) on their radiolytic decomposition to form coloured formazan. Some tetrazolium salts form colourless aqueous solutions. Upon irradiation they become permanently coloured by radiolytic reduction. It was established that the nature of solvent used and the presence or absence of oxygen affects the yield of the formazan formed. For instance, in irradiated alcoholic solutions of tetrazolium salts, the tetrazolium radicals are characterized by an intense optical absorption in the visible and UV spectral regions (Pikaev and Kriminskaya, 1998) and the yield of formazan was also found to be significantly lower in aerated alcoholic solutions compared to deaerated (e.g. N_2 saturated) solutions (Gruenewald and Schmidt-Lorenz, 1964 and Pikaev and Kriminskaya, 1995).

The basic colour change phenomenon observed during the irradiation of liquid or solid phase systems of tetrazolium salts was envisaged to be useful for dosimetry purposes and therefore different tetrazolium salts have been studied from this point of view. Gierlach and Krebs (1949) for instance studied the 2,3,5-triphenyl-tetrazolium chloride (TPTC) and observed the appearance of red colour upon exposure to UV light, as well as to α- or X-ray radiation of its aqueous solutions and gelatine emulsions. On this basis the salt was suggested for use in radiology and radiobiology to make three-dimensional dose distribution images upon X-ray treatment. It was also shown that the concentration of the formazan produced depends linearly on the dose up to about 12 kGy. The possibility of measuring absorbed doses between 1 and 16 kGy was shown by using alcoholic solutions of 0.045 M TPTC (Kovacs et al., 1995), showing a linear response between dose and absorbance at 480 nm of the triphenyl formazan product formed.

In conclusion it is noted, that different tetrazolium salts either in aqueous or in solid phase may be used for radiation processing dosimetry application in different ranges and under different conditions. As with other types of radiation processing dosimetry systems, no single tetrazolium salt has been found to be useful over a wide range of application without inherent difficulties. The need to investigate other salts of its kind to establish their unique characteristics for dosimetry application is therefore the object of this present work. Thus the aim of the investigation was to evaluate the use of tetrazolium violet (TV) in solution liquid and solid phase systems as a potential dosimeter in radiation processing applications with the following objectives:

i) to make clear the basic radiolysis processes, both electron pulse radiolysis and steady-state gamma radiolysis investigations on various aqueous and/or aqueous-ethanol solutions buffered in a wide pH range. Different radiolytic product scavengers were also applied during these studies to distinguish between oxidative and reductive processes.

ii) to achieve wider application of the system especially in electron beam radiation processing, a solid formulation (i.e. film) was prepared with a water soluble polymer matrix (i.e. polyvinyl alcohol) containing the dye.

iii) the absorbance of the irradiated solid and liquid TV systems were measured with UV spectrophotometer and most suitable evaluation conditions were addressed by the study.

iv) the dosimetry characteristics of both the liquid and solid state systems were investigated under various environmental conditions. It was necessary to determine the useful dose range of both the liquid and solid system and to study the effect of dose rate, humidity, pH, irradiation temperature on the response of the TV system whenever applicable.

v) the applicability of the liquid and film · TV dosimeter under industrial irradiation conditions and comparative study with transfer standard dosimeters for calibration of the dosimeter were established among others.

A literature review on the interaction of radiation with matter leading to radiation processing dosimetry is presented in Chapter 2. The chemistry of tetrazolium violet is discussed in Chapter 3, while Chapter 4 is dedicated to theory. The experimental methods are discussed in Chapter 5, the results in Chapter 6 and discussions in Chapter 7. The main conclusions and recommendations for further work are discussed in Chapter 8.

CHAPTER 2

LITERATURE REVIEW

Literature review

The interaction of ionizing radiation with matter leading to the types used for radiation processing is presented in this chapter. In addition the types of dosimetry systems in use for processing control, highlighting on their ranges of application and limitations are also discussed.

Interaction of ionising radiation with matter

The interaction of ionising radiation with matter involves energy transfer to the matter leading to ionisation and excitation. The imparted energy can ionise matter either directly or indirectly. Ionisation means the production of ion-pairs due to energy absorption and its direct form is due to charged particles (e.g. α - or β-radiation), while the electrically neutral neutrons and gamma rays mainly ionise matter indirectly. Beside ionisation, however, the energy of radiation transferred to the material can also cause excitation, when an atom or molecule is raised to a higher energy state, but due to insufficient energy absorption, an electron is unable to escape from its nucleus. The probability of occurrence of any particular category of interaction and the penetration power of the given radiation depends on the type and energy of radiation and on the nature of absorbing medium (Shirokov and Yudin, 1982). The intensity of ionisation along the path of an ionising particle is thus determined by the rate at which it loses energy or linear energy transfer (LET), expressed in keV per μm.

Alpha (α) -radiation

Alpha (particles) radiation is typical of elements with high atomic number (A>82). It originates from heavy radioactive nuclides and it consists of two protons and two neutrons (i.e. He nucleus). This radiation is monoenergetic with high energies (4 - 8 MeV), but its penetration is rather low (e.g. a few cm in air). This permits ionisation to occur within a given substance (solid, liquid or gas) by the formation of ion pairs due to coulombic attraction or direct collision between a traversing alpha particle and atomic electrons of the atoms within the material that the alpha particle travels. In air, alpha particles dissipate an average of 35 eV of energy per ion pair formed. The relative high mass and charge of the alpha particle in relation to other forms of nuclear radiation give it greater ionization power but poorer ability to penetrate matter. The short range of the alpha particle depends on the initial energy of the particle, the atomic number and atomic weight of the absorber and the density of the absorber. In materials other than air, such as liquids and solids, the range of alpha particles is obviously much shorter owing to their higher densities, which enhances the number of collisions a particle may undergo per path length of the travel.

Alpha particles can cause excitation and/or ionisation leading to the formation of e.g. free radicals (atoms or molecules having one or more unpaired electrons available to form chemical bonds) or other fragments resulting in chemical reactions. Though alpha particles have a high probability of interaction and are densely ionising particles (~40 000 ionisations per cm in air), they are not suitable for radiation processing due to their short range or penetration and their probability of inducing radioactivity in the irradiated material.

Beta (β) - radiation

Beta particles are high speed electrons with an initial velocity of one third to almost equal to that of light. It originates from unstable radioactive nuclei containing too many neutrons. Although the nucleus itself does not contain electrons, they are produced as a result of nuclear instability caused by the neutron/proton imbalance which results in the conversion of neutrons to protons within the nucleus, where the balance of charge is conserved by the simultaneous formation of an electron (negatron). A neutrino (ν), which is a particle of zero charge, accompanies beta-particle emission. The energies of beta particle-decay processes are usually reported as the maximum energy (E_{max}) that the emitted beta particle or antineutrino may possess. Unlike alpha particles, which have discrete energies, beta particles have a wide spectrum of energies ranging from zero to E_{max}. The majority of beta particles emitted have energies of approximately $1/3(E_{max})$.

Like alpha particles, the beta particle interacts with matter via (i) ionization and (ii) electron orbital excitation as it dissipates its kinetic energy. A third mechanism of interaction with matter, which distinguishes the beta particle, is radiative energy dissipation via bremsstrahlung production (Turner, 1995).

Collisional interactions of beta particles are somewhat different from what occurs with alpha particles. A beta particle may collide with an orbital electron or come into close proximity to it and cause the electron to be ejected, resulting in the formation of an ion pair. Considerable scattering of beta particles occurs in collision because the mass of the beta particle is equivalent to that of the atomic electron. Beta particles are therefore known as sparsely-ionising radiation (50-100 ionisations per cm in air). When electrons interact with matter they can cause secondary excitations and ionisations, producing secondary electrons (delta ray). Beta particles are easily deflected by passage through matter. Their path is not a straight line and due to scattering and their continuous energy spectrum their range is not well defined. This is in direct contrast to the alpha particle, which, for most part, retains a relatively undeviating path while passing through matter on interacting with atomic electrons.

The probability of beta particle interactions with atomic electrons increases with the density of the absorbing material. Beta particle-absorption is consequently proportional to the density and thickness of an absorber. The transmission of beta particles through an absorber may be expressed based on its exponential characteristics as follows.

$$I = I_0 e^{-\mu x} \qquad 2.1$$

where I is the intensity of the beta particles transmitted through the absorber, I_0 is the initial intensity of beta particles incident on the absorber, μ is the linear absorption coefficient in units of cm^{-1} and x is the absorber thickness in cm.

When beta particles with energies of more than 263 keV are emitted in water, or produced due mainly to the Compton effect of the interactions of gamma rays with water, they travel at a speed higher than that of light in water resulting in a bluish light, called Cerenkov light or radiation.

Beta (electron) radiation can also be produced by electron accelerators which are used in radiation processing. The accelerator utilizes electric and magnetic fields to accelerate beams of electrons. One characteristic of these electrons produced by accelerators, as against the radioisotope sources, is their narrow range of energy with a maximum at the nominal energy. Beta radiation from an isotropic source cannot penetrate matter deeply, but high energy electrons produced by accelerators have higher penetrating ability.

The induced radioactivity by beta particles or electrons as a result of nuclear reactions may be looked at as having been caused by electron "projectiles". The reaction of the knocking of a proton or a neutron out of a nucleus by an electron is highly endothermic, with a threshold of the order of 10 MeV. Below the threshold the reactions are impossible, and consequently there is no induced radioactivity. This is why for radiation processing using electron beams, the limiting energy of the electrons is 10 MeV. Electron beams are not suitable for the irradiation of thick products because of their relative short range, but accelerator produced e-beams may be used to process a relatively thick material though not as thick as would be obtained with gamma radiation. The advantage of e-beam processing is the high dose rate obtainable from machine produced e-beams which allow very high doses to be processed in a very short time. It is also important to note that such high dose rates also support the crosslinking of polymeric materials which can only be achieved with difficulty for gamma sources.

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Gamma and X-ray radiation

Radionuclide decay processes often leave the product nuclide in an excited energy state which either falls directly to the ground state or descends in steps to lower energy states through the dissipation of energy or gamma radiation. The monoenergetic gamma rays therefore originate from the nuclei, accompanying nuclear transitions. The energy of the γ-rays (in the range of keV to MeV) is emitted as photons in discrete energies corresponding to the energy state transitions a nuclide may undergo when in an excited state.

$$E_{\gamma} = h\nu = E_1 - E_2 \qquad 2.2$$

where $h\nu$ is the energy of the electromagnetic or gamma radiation and E_1 and E_2 represent the energy levels of the nuclear isomers.

X-rays arise from reactions outside the nucleus, accompanying electronic transitions. Electron capture and internal conversion lead to monoenergetic X-rays, while the continuous energy X-rays - called bremsstrahlung - are produced when electrons of high energy lose their energy in passing through matter. Bremsstrahlung is produced in X-ray machines and in electron accelerators.

Electromagnetic radiation interacts with matter in an indirect way, i.e. producing secondary electrons and photons of lower energies, which are then the ionising particles. A photon can interact with matter by several mechanisms, i.e. with the entire atom (photoelectric effect and Rayleigh scattering), or with one electron in the atom (Compton effect which occurs in the field of an electron), or with the atomic nucleus (pair production). Photons of energies below 0.5 MeV may completely be absorbed transferring their energy to an electron of one of the innermost orbitals, which is then ejected (photoelectric effect). Higher energy photons (0.5 - 1 MeV) may collide with the loosely bound orbital electrons. These photons are then deflected and their energy reduced by the amount of energy which was given to the electrons (Compton electrons), ejected afterwards. High energy photons (>1.02 MeV) may react with the electric field around the nucleus and convert all their energy to the production of an electron and positron (pair production, using 1.02 MeV).

In photoelectric effect, the energy of the emitted electron is equal to the energy of the impinging photon less the binding energy of the electron i.e.

$$E_e = h\nu - \phi \qquad 2.3$$

where E_e is the energy of the ejected electron, $h\nu$ is the energy of the incident photon, and ϕ is the binding energy of the electron or the energy required to remove the electron from the atom. The ejected electron is similar to a beta particle and produces ionisation (i.e. secondary ionisation) as it travels through matter as previously described for beta particles.

For Compton effect, the gamma photon E_γ only imparts a fraction of its energy to the electron and gets deflected with energy $E_{\gamma'}$ at an angle of Θ, while the bombarded electron is ejected at an angle of θ to the trajectory of the primary photon. The energy lost by the incident photon according to the Einstein-Planck relation is given by

$$\Delta E = E_{\gamma} - E_{\gamma}^{'} \qquad 2.4$$

The absorption of electromagnetic radiation is exponential, i.e. it can never be completely stopped. The gamma radiation has a low linear energy transfer (LET) resulting in more penetration, than that of alpha and beta radiations. The absorption of gamma rays by matter obeys the fundamental Lambert-Beer law:

$$I = I_0 e^{-\mu x} \qquad 2.5$$

In this equation I and I_o are the intensities of transmitted and incident radiation respectively, x is the thickness of the absorber and μ is the linear absorption coefficient.

Radiation sources for radiation processing

The common forms of radiation employed in the radiation processing industry are:

i. gamma rays emitted by radioisotopes ^{60}Co (having a mean energy of 1.25 MeV) and ^{137}Cs (with energy of 0.66 MeV). The use of ^{137}Cs for radiation processing is being discouraged because of high self absorption in the source pencil due to its low energy, and the fact that the powdered CsCl is very soluble in water binging about a high probability of contaminating the water pool if there is any corrosion;

ii. electrons generated from machine sources in the energy range of 0.15 – 10 MeV;

iii. X-rays with energy at or below 5 MeV. Bremsstrahlung X rays are produced whenever accelerated electrons are slowed down or stopped in high atomic-number metal target (i.e. the converter). The relatively low efficiency at which electrons create bremsstrahlung has so far limited the industrial interest in this source of radiation. The recent appearance of very powerful electron accelerators has, however, renewed the interest and X-ray sources may be more widely used in the future.

One of the main reasons why these types of radiation have been chosen for radiation processing lies in their nature and energy, and that they do not induce any radioactivity in the irradiated material. The choice of which to use for a given commercial process is largely a matter of economics and the type (size and density) of the products being irradiated. Beyond those two factors the effects of either γ or X-rays or electron beams on a material are much the same. Any differences which may be observed from irradiating a material with γ or X-rays instead of electrons are mostly due to differences in the amount of energy absorbed by the material, and therefore related to the penetration power of that particular radiation type, since the various types of radiation give different depth-dose profiles.

Basics of radiation processing

As discussed earlier, radiation processing is the use of high energy (0.1 - 10 MeV) ionising radiation to achieve certain technological purposes like sterility of medical devices, crosslinking of polymers, surface treatment, etc. Radiation processing is relatively a young industry, which during the past few decades has shown significant development and progress in a few fields. At the same time the introduction of new technologies e.g. in biomedical applications and in environmental protection, is also expected in the near future.

The technological use of ionising radiation leads to the development and enhancement of the quality of certain materials and the production of new materials. It also improves the efficiency of some processes as in decreasing the energy required for the vulcanisation of natural rubbers (latex). One other advantage of this technology is the available use of various standardized dosimetry systems as suitable and independent process control methods. The wide-spread use of these technologies is shown by the fact that about 800 electron accelerators and more than 200 high activity gamma radiation facilities are in operation around the world, both in developed and developing countries. Radiation processing technologies can be put into three categories namely;

i Established technologies as in radiation sterilization, crosslinking, curing, grafting, vulcanisation and degradation;

ii. Emerging technologies as in food irradiation, environmental applications like in treatment of drinking water, municipal waste, industrial waste, radiation modification of semiconductors and decontamination of animal feed;

iii. New developments as in radiation bioengineering for the synthesis of biocompatible materials, immobilisation of bioactive materials, biomass conversion and in the viscose industry (Ottavio Barnabel, 1998).

Established technologies

The radiation sterilization of single use medical devices is already in use in more than 50 countries around the world. More than 60 % of these devices are sterilized by ionising radiation in the USA, Japan, and the European Union and in Ghana since 1994. The role of this technology is increasing in other parts of the world by the day.

Ionising radiation is used to produce various polymer products of new characteristics. Radiation crosslinking transforms a linear polymer into a three-dimensional macromolecule resultant product of improved mechanical and electrical properties (like tensile strength), as well as of improved thermal stability. This technology needs less energy compared to the conventional methods and is cost effective where large volumes of products are produced. Radiation crosslinking is used to produce heat-shrinkable materials, insulation for wires and cables, foamed polymers, vulcanized tyres and composites. Radiation curing consists of the simultaneous radiation induced polymerization and crosslinking of monomers and/or oligomers on products like paper, plastic films, wood panels, metal sheets and ceramics. Thus radiation processing has got application among others in the building industry, production of furniture components, in offset printing, magnetic media coatings to produce floppy discs and videotapes. Grafting consists of the addition of a monomer or oligomer onto a backbone polymer resulting in a new polymer material with new surface or bulk properties. Radiation processing technology is also employed in the textile industry to produce materials of improved ability to absorb dyes and reduced electrostatic charges as in polyacrylonitrile fibres. The production of aluminium foils coated with polyethylene grafted with acrylic acid for wrapping materials and the manufacture of ion-exchange membranes utilizes this technology too.

Radiation degradation utilizes that effect of radiation on some polymers which undergo chain scission leading to reduction in their molecular mass. This process, in combination with other treatments, is used to degrade agricultural and industrial waste containing cellulose. The high dose irradiation of teflon (few hundred kGy) to powder results in valuable additives applicable for instance in ink production. Radiation degradation has recently found use in the viscose process resulting in the use of less toxic chemicals and decreased energy consumption by about 10 %.

New technologies under establishment

The use of ionising radiation in environmental protection is a new field, where usually radiation technology is applied or in combination with others to achieve cost effective applications. Some of such technologies are already in pilot or industrial scale application:

- treatment of natural and polluted drinking water;
- decontamination of industrial and municipal wastes and sewage sludge; and
- purification of flue gases of power plants containing sulphur and nitrogen oxides responsible for the “acid rain” which leads to the destruction of forests.

These technologies do not only result in the decrease of environmental pollution, but also may lead to useful by-products as well, like animal feed and fertilizers (Ottavio Barnabel, 1998).

The radiation treatment of food, although has a long history, seems to have just received real industrial application. Extensive research over more than five decades has proved the usefulness and safety of food irradiation. Based on these results, the WHO, FAO and IAEA in a joint recommendation approved and suggested the irradiation of various foodstuffs up to 10 kGy (Joint FAO/IAEA/WHO Expert Committee on the

Wholesomeness of Irradiated Food (JECFI) and the Codex Alimanterius, 1983). Later the upper dose limit was changed giving the possibility of irradiating food up to very high doses where the limitation factor is only the quality of the product. So far only the irradiation of spices to reduce microbiological contamination and the inhibition of sprouting has got industrial scale application. The recent governmental approval of the radiation treatment of meat and poultry and the disinfestations of fresh and dried fruits in the USA will probably change the public attitude and perception of irradiated foods which delayed the large scale application of these technologies worldwide. Currently about 30 commercial and pilot scale gamma and electron beam irradiation facilities are used to treat food worldwide. These recent approvals have given rise to the design and development of new food irradiation facilities.

The use of ionising radiation in the semiconductor industry has to be mentioned for completeness, since the electron irradiation of certain types of diodes, thyristors and transistors improve their functional parameters, like switching time as used in electric engines. The advantage of this technology over the traditional diffusion technique is the better distribution and lifetime of the charge carriers.

New developments

New achievements include the production of biomedical products like hydrogel-like-synthetic wound dressings and bio-compatible material drug release systems. The viscose technology and the production of heat resistant SiC filaments belong also to the new achievements.

Irradiation facilities

Industrial irradiation technologies use either gamma radiation of radioactive isotopes with energies less than 5 MeV or electron accelerators producing electrons in the energy range of 100 keV - 10 MeV.

The gamma irradiation facilities usually employ ^{60}Co isotope, and in a few cases ^{137}Cs. There are different types of gamma irradiation facilities for radiation processing. Container type irradiators are used for research and calibration purposes, while pilot scale facilities, like the panoramic irradiators at Kwabenya-Ghana are designed both for research and small scale industrial applications. Industrial scale facilities contain high activity sources (1 - 100 PBq) arranged in plaque or cylindrical form and the irradiation of big volume products is carried out around these sources with various type product transport systems.

The energy range (0.1 - 10 MeV) of electron beam irradiation produced by accelerators of different power (1 - 300 kW) depends on the technological application of the facility (Zimek, 1991). In general the accelerated electrons are scanned perpendicularly on the product. The low energy, high current machines are usually applied for surface treatment and crosslinking of polymer products, and in flue gas treatment while accelerators of 4 - 10 MeV energy are used for sterilization of medical supplies and for food irradiation purposes. Electron accelerators are also used for the production of X-rays, which have much higher penetration, than the electron beams from accelerators. Due to the low production efficiency of X-rays, on the other hand, its present industrial scale development and application has just begun.

Role of dosimetry in the quality control of radiation processing

Dosimetry plays a key role in the quality control of radiation processing activities. This fact has also been recognized by the International Organization for Standardization (ISO) and has instituted quality control systems -first for the sterilization of medical devices, and then for other technologies, like food irradiation, polymer modification - based on standards developed by the ISO and, ASTM (American Society for Testing and Materials) among others (IAEA Tech. Report Series 409, 2002). It is required, that all dosimetry measurements are traceable to national or international standards, and the uncertainty of these measurements must be stated with appropriate confidence limits. It is of basic significance, since beside the control of machine parameters - correct absorbed dose measurements provide the independent proof that a process has been carried out according to specifications. In quality assurance programme, radiation dosimetry plays a key role in the following procedures (ISO/ASTM 51702:2004):

- Characterization of irradiation facilities (i.e. operational qualification) – to establish relationship between facility;
- parameters and dose absorbed in the product;
- Product and performance qualification - to establish irradiation parameters for the given product including the measurement of dose distribution within the product package;
- Determination of minimum and maximum dose values and their locations in the products; and
- Routine dose control - to check absorbed dose at reference positions on or in the product at regular intervals.

Determination of absorbed dose

The energy deposited by ionising radiation in matter, i.e. the absorbed dose is measured by dosimeters placed in the material. The absorbed dose, D, is the amount of energy (*d*E) absorbed per unit mass (*d*m) of irradiated matter at a point in the region of interest:

$$D = -\frac{dE}{dm}(Gy) \qquad 2.6$$

As discussed earlier it has been established that the absorbed dose depends on the energy and type of the radiation, as well as on the atomic composition of the absorbing matter. The dose absorbed in two different materials can be different even if both materials are exposed to the same radiation field for the same time. Hence, the dosimeters to be applied are selected according to the composition of the products to be irradiated. Some of the dosimeter systems (water or plastic based ones) applied in radiation processing - like many products (polymers, foods) - are water equivalent, i.e. their radiation absorption properties are similar to water. Thus the energy absorbed by the product can be well approximated to the dose measured by the dosimeter (IAEA-Technical Reports Series 409, 2002).

Alternatively, the dose measured in one material can be calculated into another material of different radiation absorption characteristics by using correction factors. Since the composition of the dosimeter is generally different from that of the absorbing material with respect to both density and atomic number, there comes into play “discontinuity” in the material, called “cavity”. The relationship between dose absorbed by the dosimeter (D_d) and by the surrounding material (D_m) can be described by the following equation:

$$D_m = \frac{1}{f} D_d \qquad 2.7$$

where “f ” is the correction factor both in the case of gamma and electron radiation, which has to be determined for the dosimeters.

Requirements concerning the performance of dosimeter systems and their selection criteria

When selecting a dosimeter system for the control of an irradiation technology, it is of basic importance to consider the type of radiation processing procedure to be controlled. In all cases dosimeters have to be calibrated against primary or reference standard systems.

Requirements for the selection of reference dosimeters

The use of primary or secondary reference standard dosimeters is based on the measurement of basic physical (ionisation current, temperature, electric charge, etc.) or chemical (G-value of radiolytic products, absorbance, luminescence, etc.) parameters. In the case of the reference standard dosimeters, the relationship between the radiation induced change and the absorbed dose can be measured accurately. Hence these dosimeters which are used mainly for calibration of routine dosimeters are first calibrated against standard systems at primary or reference laboratories. Although different systems are known for this purpose (e.g. calorimeters, ionisation chambers) due to energy dependence problems calorimetry is the typically applied system at higher doses. The main requirements concerning the use of these systems are:

1. High accuracy and reproducibility (± 1 - 2 %);

2. Long term stability both before and after irradiation;
3. Exact knowledge of all relevant environmental effects;

The transfer standard dosimeter systems (± 3 %) can be applied both for calibration, intercomparison and routine dose control. The use of these systems is based on the reproducible, accurate measurement of radiation induced changes (absorbance, ESR-signal) among others, which require calibration.

Requirements concerning the use of routine dosimeters

When selecting routine dosimeters or when studying a system for use as a routine dosimeter for dose control in radiation processing the following criteria are used to achieve the basic requirements and confidence in the dosimetry for quality control/assurance:

- Calibrated and stable response over a specified dose range at a given radiation energy;
- Good reproducibility of dose effect (response) and its measurement at the required dose levels;
- Limited energy dependence of response;
- No variation of response within the relevant dose-rate range;
- Product equivalent radiation absorption characteristics (water equivalence);
- Limited (and known) variation of response with environmental conditions (light, temperature, humidity, impurities, storage);
- Simple, standardized and cheap read-out procedure;
- Low cost and simple handling and read-out procedures;

- Specified size;
- Batch-to-batch stability;

The purpose and importance of technological (process control) dosimetry

The purpose of the application of technological/process control dosimetry in radiation processing is the determination of technological parameters as well as the measurement of dose distribution within the product during product validation on one hand. On the other hand its proper use during routine operation serves as an independent tool for quality assurance.

Calibration

Calibration involves establishing the relationship between the absorbed dose and the radiation induced effects in dosimeters determined using the measurement instrument. The calibration procedure of a dosimetry system mainly consists of (ISO/ASTM 51702:2004):

(a) Irradiation of dosimeters to a number of known absorbed doses over the useful dose range; (taking note that it is necessary to calibrate the dosimeters in a wider range than the expected range of use!);

(b) Analysis of the irradiated dosimeters using the calibrated measurement instrument;

(c) Generation of a calibration relation (curve);

Such a calibration must be traceable to a national or international standard, which means that the measurements are certified by the national or international laboratory.

Primary and secondary standards dosimetry laboratories, as well as accredited laboratories possess methods and instruments, which can measure absorbed dose with suitable accuracy and reproducibility. The role of these laboratories is of basic significance concerning the proper dosimetry procedures carried out at the industrial irradiation facilities due to calibration requirements. Calibration may include reference irradiation of routine or reference dosimeters at precise dose values. Laboratories must be accredited according to ISO requirements to be able to provide calibration services (Sharpe, 1999).

Dosimetry control at radiation processing technologies

The validation of a new product to establish or set the irradiation parameters involves establishing the dose required to achieve the set objective and the determination of dose distribution in the product package after a full irradiation run. In the case of gamma irradiation the dose distribution can be measured with routine dosimeters of suitable accuracy by placing them in the product package in a "matrix form". In the case of electron beam irradiation, film dosimeters are applied for dose distribution measurements in which case the size (and the special evaluation, i.e. scanning densitometry) offers the best resolution. After having measured the dose distribution within the product package it is possible to determine the minimum and maximum dose values, their respective locations and to set the technological parameters of the irradiation process (i.e. dwell-time, conveyor speed etc.) depending on the product density, type of irradiation facility and the required minimum dose. After the validation of the given product, dosimetry plays an equally important role during the routine control of the irradiation technology by establishing whether or not the product has been irradiated according to the established specifications, i.e. within the specified dose limits. The accuracy of routine dosimetry or tolerance in the course of sterilization of medical products and food irradiation usually should be within 10 %. During the calibration of these routine dosimeters the required accuracy limit is set at ± 5 %, which includes both the irradiation and evaluation uncertainties (ISO/ASTM 51702:2004).

Radiation processing dosimetry methods

One possibility of categorizing radiation processing dosimetry systems is based on whether chemical or physical changes are caused by the ionising radiation during their interaction with the dosimetry system. In the present work the chemical changes occurring in the organic compound is the object of the investigation.

Physical methods of dosimetry

The basic principle concerning the use of the physical methods is the measurement of radiation induced changes of such physical quantities as temperature, ionisation current or electric charge etc.

Calorimetry

Calorimetry is an absolute standard method, where the energy absorbed in the calorimeter body from radiation is almost entirely converted into heat and the temperature change is the measure of absorbed dose. In practice there are complex arrangements with adiabatic enclosures, containing reference cells and calibration heat sources, while on the other hand relatively simple quasi-adiabatic designs, called process calorimeters may be used. In electron beam radiation processing applications the latter design is mainly employed. These systems consist of an insulated calorimeter body (e.g. a polystyrene Petri dish containing water, or a graphite disc or a polystyrene disc) and a thermistor or thermocouple to measure the temperature rise in the calorimeter body. The insulation is usually made of polystyrene foam (Miller A., 1995; Domen S.R and Ba W. Z, 1987). The absorbed dose is calculated by multiplying the temperature rise (ΔT) with the specific heat of the absorber. The measurement uncertainty of calorimeters depends on the specific heat of the calorimeter body and the calibration range of the thermistors (e.g. maximum 55 ^{o}C) and the acceptable value of measurement uncertainty. (i.e. the dose range depends on the specific heat). For instance graphite cannot be used above approximately. 15 kGy due to melting of the foam insulation. These process calorimeters can be used in the $10^2 - 10^5$ Gy dose range (International Atomic Energy Agency, Tech. Rep. Series 40a, 2002) with an overall measurement uncertainty within ± 5 % at a 95 % confidence level. These types of calorimeters are in use in the 4 - 10 MeV electron energy range, but new, thin polystyrene calorimeters have recently been designed and tested for application in the energy range down to 1.5 MeV (Miller A. and Kovacs A., 1985, ASTM E1631, 2000). Due to the nature of these calorimeters, however, each type is calibrated by transfer dosimetry when used for routine dosimetry. The routine application of these calorimeters is limited to electron radiation processing, since the long irradiation time in gamma facilities militates against their reliable use. Their dosimetry application in electron beam facilities involves nominal dose measurements during facility qualification, product validation and the calibration of other routine dosimeters.

Ionisation methods

Ionisation chambers are mainly used in radiation therapy and radiation protection as primary and secondary standard systems and the method is considered as one of the most accurate ones to measure small doses by using different volumes of cavities filled with different gases at known pressures and measuring the ionisation inside these cavities.

Their use is based on the Bragg - Gray theory, which stipulates that, provided the cavity is small with respect to the range of secondary electrons, the rate of energy absorbed per unit volume of the wall material, is equal to the product of the ionisation current produced per unit volume of gas in the cavity. Thus this theory provides a means of relating ionisation measurements in a gas to dose absorbed in a suitable material of which the dosimeter is fabricated. Various types of ionisation chambers have been developed for measuring high absorbed dose rates in nuclear reactors, accelerator beams and photon fields.

Semiconductors

Semiconductors (like silicon diodes) can be used for dosimetry and for dose mapping in radiation processing. When semiconductors are exposed to ionising radiation, electric current is produced across the p-n junctions due to the diffusion of electron-hole pairs from the depletion zones to the p and n layers and this current measured in the so-called short-circuit mode can be used for dose rate measurements.

Semiconductors are mainly used for the determination of dose rate in steady-state fields (e.g. in research irradiators) and for mapping of dose fields. Recent investigations have shown, that silicon devices (e.g. bipolar power transistors), can be considered for dose determination mainly in electron processing in the range of 0.1 - 5 kGy and in the energy range of 2.5 - 12 MeV. The advantages of the use of these devices are their small size, low cost, simplicity of use, non-destructive nature of use of the semiconductors i.e. possibility of reuse. On the other hand, the response of the detectors depends on energy and temperature which is a setback in the overall application of semiconductors for routine dose control.

Chemical methods of dosimetry

The chemical methods of dosimetry are applied by measuring reproducible chemical changes caused by ionizing radiation. Apart from the physical systems, most dosimetric systems are chemically based. However some are used in the liquid form whilst others are used in the solid phase. The characteristics of the important chemical dosimetry systems are discussed in detail in Dosimetry for Food Irradiation by IAEA Techncial Report Series 40a, (2002). In the following paragraphs the characteristics of the most important systems, relevant to the topic of this thesis, will be discussed.

Solid phase systems

Most of the solid dosimeter systems used in radiation processing consist of either organic or inorganic crystalline materials or quasi-crystalline and amorphous materials. The radiation induced change as a measure of absorbed dose is measured by different analytical methods like spectrophotometry, electron spin resonance (ESR) technique (Regular and Deffner 1982), optically stimulated luminescence, conductivity (Kovacs et al., 1995; Kovacs et al., 2000).

Electron Spin Resonance (ESR) evaluation, also called Electron Paramagnetic Resonance (EPR) has long been used as a quantitative tool to study the effects of radiation. Ionizing radiation produces free radicals in many forms of matter that can be quantitatively detected by an EPR spectrometer. The EPR spectrometer works by measuring energy level transitions of unpaired (free) electrons at a specific resonant frequency within a variable magnetic field. In crystalline organic compounds (like amino acids) free radicals are produced by radiation and since the concentration of these radicals is stable for long periods and easily measurable, it is suitable for dosimetry applications using ESR method. Alanine forms a very stable free radical when subjected to ionizing radiation. The alanine free radical yields an EPR signal that is dose dependent, yet is independent of the dose rate. As a result of several investigations the crystalline α-L-alanine has been found most suitable for dosimetry purposes due to its wide dose range (1 - 10^5 Gy), accuracy and reproducibility (ASTM E1607, 2001). The method is now mainly used at calibration laboratories as a reference standard system and also as a transfer standard system for the calibration of routine dosimetry systems at industrial processing facilities. It is used nowadays in gamma and electron processing applications (in pellet, rod or film form), but its introduction for medical and environmental control purposes is also under investigation.

The dosimeter is produced with different binders (e.g. paraffin, cellulose, polystyrene) or suspended in various polymers for film formulations. The nominal absorbed dose range is 1 - 10^5 Gy with linear response up to about 10^4 Gy. The signal measured is the amplitude of the first derivative of the ESR spectrum, which is proportional to the weight of the sample. Due to relatively insignificant fading of the irradiated dosimeters the system is one of the few dosimeters, which can be re-measured even many months after irradiation (i.e. non destructive system), which is important from quality assurance point of view. No significant dose rate dependence of the dosimeter has been reported up to about 10^8 Gy s^{-1}, but humidity, temperature effects above 50 °C and UV light can cause problems and may need correction (Sleptchonok et al. 2000 Nagy et al., 2000). The irradiation temperature effect is taken into account by using the relevant correlation coefficient, which is dependent on the dose level. The disadvantage of this method is the expensive ESR spectrometer, which limits the routine use of the system. It must be mentioned, however, that this system has been selected by the International Atomic Energy Agency as a transfer standard system for the International Dose Assurance Service (Mehta and Girzikowsky, 1999).

To avoid the use of ESR analysis due possibly to the expensive spectrometer, Gupta and co-workers (1985), developed the chemical analysis of the irradiated alanine (and glutamine) dosimeters by dissolving the irradiated dosimeters in an acidic solution containing Fe (II) ions. During dissolution the free radicals of alanine oxidize the Fe (II) ions producing Fe (III) ions, which then give a complex with the xylenol orange. The optical absorbance of this complex (i.e. which is related to absorbed dose) is measured at 525 nm. The routine use of the system is somewhat time consuming and therefore not really practicable for industrial irradiation processing.

The optical absorption spectra (or colour) of many solid state dosimeters change due to the effect of ionising radiation and this effect is utilized for dose measurement. In some solid materials unsaturated bonds appear due to irradiation, resulting in optical bands absorbing in the UV range. In other cases the dosimeters contain some dyes resulting in colour changes upon irradiation, which is utilized for absorbed dose measurements. The characteristics of these systems include their simplicity in use and evaluation, but in most cases their reproducibility are affected by such environmental conditions, as humidity, light, temperature and the presence of oxygen. Therefore the use of such systems requires great care and the need to apply the necessary correction factors.

Different types of polymethylmethacrylate (PMMA) dosimeters are in use for radiation process control as routine dosimeters. Radicals are produced by radiation resulting in optical absorbance change, but the concentration of these fragments change with time due to various environmental factors. With each type of perspex system it is advisable to carry out the measurement a few hours after irradiation due to significant changes of absorbance immediately after irradiation (McLaughlin et al., 1977).

The practical importance of HX-Perspex (“clear Perspex”) dosimeter has decreased significantly due to its post irradiation instability. The fading characteristics are a complex function of temperature, time, dose and wavelength. The most stable wavelength for measurement is at 315 nm, but still care has to be taken when in use. The most frequently used Perspex system is the red Perspex, which is applied in the sterilization dose range (5 - 50 kGy) by measuring the absorbance at 640 nm preferably a couple of hours after irradiation. The amber Perspex dosimeter is used in the dose range of 3 - 15 kGy (651 nm), while the Gammachrome was developed for lower dose measurements (0.1 - 3 kGy) at 530 nm.

For all types of dyed perspex dosimeters the specific absorbance (i.e. absorbance divided by the thickness of the dosimeter) is related to absorbed dose showing a non-linear response. It is characteristic of their post irradiation behaviour that after irradiation there is an increase of the absorbance, which after a few days tends to decrease depending on environmental effects like humidity and temperature. These conditions influence the behaviour of these dosimeters both during irradiation and storage. Some of these effects can be suppressed by storing the dosimeters in three layer pouches until the spectrophotometric evaluation. Nevertheless all these factors must be kept in mind when using this family of dosimeter.

Cellulose triacetate (CTA) films have been developed for measuring higher doses (i.e. 25 - 200 kGy) by evaluating the irradiated films at 280 nm (Janovsky and Mehta, 1994). The film is produced with a plasticizer, which also helps the stabilization of the absorbance after irradiation. When applied it must be noted that its response is different for gamma and electron irradiation due to dose rate differences, stemming out of oxygen diffusion. Immediately after irradiation the film has a strong fading (~ 20 %) for about 15 minutes followed by a slow increase (~ 10 - 20 %) in absorbance for several days. Thus its post irradiation instability must be taken into account with respect to calibration and routine application. Its response is also affected by humidity and temperature variation during irradiation and requires care concerning its analysis due to the steep edge of the absorption band at which the evaluation is done.

Radiochromic films have got wide-spread application in radiation processing both in gamma and electron irradiation and due to their size and spatial resolution, their use is of additional specific significance in dose mapping of electron beam irradiated products.

The nylon based, colourless, thin (50 μm) *FWT-60* film containing hexahydroxyethyl pararosaniline cyanide (produced by Far West Technology, USA), becomes deep blue upon irradiation in the dose range of 3 - 100 kGy. Its absorbance is measured either at the peak of absorption (605 nm) at lower doses, while at higher doses (> 30 kGy) the evaluation is carried out at 510 nm. Its response is independent of the energy and type of radiation, but the effect of irradiation temperature, humidity and light - especially UV light - must be controlled. Due to potential thickness variation the specific absorbance is used instead of the absorbance. The colourless polyvinyl butyral based pararosaniline cyanide containing *B3 film* (20 μm) is changed to pink upon irradiation. It is applicable in the 5 - 200 kGy dose range by measuring the absorbance at 554 nm. It is characteristic of these films that the absorbance increases for several hours after irradiation. This effect is eliminated by using a heat treatment of the irradiated films (i.e. keeping it at 60 °C for 5 minutes) to stabilize the film. Its application needs special care due to its very thin size, although a recent commercial product using the film in a paper holder seems to be free from this problem. Environmental factors like humidity, UV light and temperature affect the response of the film, thus special care is again required.

Another film of interest is the *GafChromic* dosimeter, which was developed mainly for low dose measurements, but the determination of high dose is also possible (10 Gy - 40 kGy) by carrying out the evaluation of the irradiated film at various wavelengths (670 nm, 580 nm, 400 nm). This dosimeter is different from the others, since the radiation sensitive radiochromic layer (7 μm) is coated on a polymer material, which eliminates the measurement of thickness. The use of the film is limited to irradiation temperatures below 60 °C due to modification in the lattice. When considering the use of this film, humidity, dose rate and light have to be considered due to their effect on the response of the film.

The measurement of luminescent light originating from irradiated crystalline materials is the basis of the determination of absorbed dose using various techniques and materials.

Thermoluminescence (TL) is used for the determination of absorbed dose by utilizing the phenomenon, by which charge carriers (electrons and holes) produced in the irradiated crystalline material and trapped by impurities or imperfections in the lattice are released during the heating of the irradiated crystal. Their recombination results in an emission of measurable light characteristic of the absorbed dose. These dosimeter systems are mainly applied in low dose ranges (mGy region), but a few systems can be applied even in the kGy range, i.e. in radiation processing. One of these systems is the LiF dosimeter, which is applicable up to about 100 Gy being useful for dose control in disinfestations.

Lyoluminescence (LL), is the phenomenon by which measurable light, used for dose determination, is emitted upon dissolution of irradiated crystalline materials in a solvent. The luminescence is due to chemical reactions of the stable radiation-induced free radicals with the solvent. The emitted light is integrated during dissolution (for about 20 - 30 sec) and related - by calibration - to absorbed dose. Such systems are e.g.

glutamine, valine, phenylalanine, but this method has not become a routine one in radiation processing due to its complicated application procedure.

A recently improved method is based on the measurement of optically stimulated luminescence (OSL), in which visible or UV light is used to excite the irradiated dosimeter material resulting in the emission (luminescent light) used for dose determination. The basic principle is that the wavelength of excitation and emission should be significantly different to avoid overlapping.

A new promising dosimeter system developed recently based on this principle is the *Sunna film*, which contains LiF in a polyethylene matrix (Kovacs et al., 2002). The film is applicable in the 10 Gy - 200 kGy range covering various applications in radiation processing. Using OSL evaluation the emission is measured either at 550 nm (green) or 670 nm (red) after an excitation at 450 nm. IR emission at around 1000nm with excitation at around 600 nm seems also suitable. The advantage of this non-destructive method is its simplicity, fast evaluation and wide dose range. According to recent investigations the measurement of the green emission eliminates most of the irradiation temperature effect for practical application. The advantage of the film is its homogeneous thickness, but its post irradiation stability and the irradiation temperature effect (red emission) must be controlled and taken care off. Another advantage of the Sunna film is that it can also be used with spectrophotometric evaluation by measuring the absorbance of the irradiated film at 240 nm and evaluating dose in the 5 - 100 kGy range.

Liquid phase systems

Ionising radiation loses its energy in liquids by interactions with atoms and molecules leading to the formation of chemically active species such as solvated electrons, ions, free radicals and radical-ions. These species react with each other and with the surrounding molecules (e.g. solvent) resulting in chemical changes which are utilized in radiation dosimetry. The time-scale of these reactions are different and can be shown in the case of water as a frequent solvent in radiation dosimetry. Ionisation and excitation happens within 10^{-15} sec followed by the thermalization and hydration of the ejected electrons (10^{-12} sec). Proton transfer resulting in hydroxonium ions (H_3O^+) is also a fast process (10^{-14} sec) in some dosimetry systems applied in radiation process control. Hydrogen atoms and hydroxyl radicals are produced from the dissociation of excited water molecules on a fast time-scale (10^{-13} sec) as some of the most important species in aqueous dosimetry systems. All these species (e^-_{aq}, OH, H, H_3O^+, H_2, H_2O_2) are also the products of the reactions of the primary radiolysis species with each other on nanosecond time-scale (Spinks and Woods, 1990). The reactions of the radiolytic products of water with solutes lead to the formation of such products, which can be used in dosimetry by measuring their concentration, i.e. measurable and reproducible chemical changes are utilized for dosimetry purposes. The systems used most widely in radiation processing are discussed below.

The Fricke solution (i.e. secondary standard dosimeter system) is frequently used for the dose rate determination of irradiation fields, dose control of irradiation technologies and for the calibration of routine dosimeters. It is mainly used for gamma and X-ray radiations, but in certain cases it is also applicable for dose determination in electron irradiation fields as well. The basic principle of the system is the oxidation of Fe^{2+} to Fe^{3+} in acidic, aqueous, aerated solution; the concentration of the ferric ions being determined by spectrophotometry at 304 nm for the dose determination. The disadvantage of the system is the narrow dose range (20 Gy - 400 Gy), where the lower limit is set by the limits of the analytical method, while the upper one is due to oxygen depletion. The advantage of the system is its accuracy, precision and relative simplicity of use if care is taken to avoid the effects of impurities. The dosimeter solution is nearly equivalent to water and biological tissues in terms of photon and electron absorption properties.

The use ceric-cerous aqueous dosimeter is based on the radiolytic reduction of ceric ions to cerous ions in acidic environment. The concentration of the Ce (III) ions is determined by spectrophotometry at 320 nm and the useful dose range is 1 - 200 kGy. Since the solution is very sensitive to impurities the modified composition of the solution, i.e. the addition of cerous ions leading to a ceric-cerous system was introduced. The evaluation of this solution is also carried out with potentiometry ASTM E51205 2002. The modified composition improved the dosimetry characteristics of the solution, while the potentiometric analysis improved its use in practice.

One of the methods suggested recently as a reference/transfer standard method is the aqueous, acidic potassium dichromate solution, the use of which is based on the radiolytic reduction of Cr (VI) ions to Cr (III) evaluated at 440 nm by UV spectrophotometry. The detailed study of the system was discussed by Sharpe (1999), who described its application in detail and suggested its use as a reference standard method in the 10 - 40 kGy dose range mainly in gamma radiation processing. Using a modified composition and a different measurement wavelength, it is also possible to measure doses in the range of 2 - 10 kGy. The preparation of the solution requires extra care due to the effects of impurities, while during storage light effects must be avoided.

The ethanol chlorobenzene dosimeter provides a reliable means of measuring absorbed dose based on the process of radiolytic formation of hydrochloric acid (HCl) in aqueous ethanolic solutions of chlorobenzene. This dosimeter is an aerated organic chemical system, where the monochlorobenzene is dissolved in ethanol containing also a small amount of distilled water. (i.e. small amounts of acetone and benzene against impurities is not needed according to recent studies). Upon irradiation, the concentration of HCl formed is proportional to the absorbed dose in the range of 0.4 - 300 kGy. The measurement of absorbed dose can be achieved by using different evaluation methods:

(a) mercurimetric titration is used to determine the chloride ion concentration and calculating the dose by using the predetermined $G(Cl^-)$ value; thus the method can be considered as a secondary standard method. It is however, time consuming and therefore not practical for industrial purposes.

(b) high frequency oscillometric measurement of the irradiated solution utilizes the change of the conductivity of the solution and the measurement is performed in a sealed ampoule thus making possible the re-evaluation of the solution at sometime later (non-destructive method).

Oscillometry is an electroanalytical method, with the ampoule containing the solution to be measured (i.e. ECB solution) placed between the electrodes of a high frequency oscillator resulting in the change of its voltage due to the variation of the conductance or Q-factor of the irradiated solution. The oscillomteric method is a widely applied routine dose control method, which needs calibration. Under careful application conditions, however, the method was also suggested as a transfer standard system in radiation processing in the range of its applicability (1 - 300 kGy).

The advantages of this dosimetry system among others involve the resistivity of monochlorobenzene against oxidation, the fact that ethanol is a good inhibitor of chain reactions and good solvent for HCl, which is in the dissociated form in the solution. The solution is also not sensitive to impurities. By changing the concentration of monochlorobenzene (4 - 40 vol. %) the radiation absorption characteristics of the solution can be matched with that of the products. Another important feature of the system is that its response depends very little on the irradiation temperature and on the energy of photons and electrons, but the effect of UV light must be avoided during storage and irradiation.

CHAPTER 3

CHEMISTRY OF TETRAZOLIUM SALTS

Chemistry of tetrazolium salts

The structure of the tetrazolium salts, their associated reduction process and the dosimetry characteristics of those investigated are discussed among others to bring out the need to study 2, 5-dipheny-3-(1-naphthyl)-2H-tetrazolinum Chloride (TV) for use in radiation processing dosimetry.

The chemistry of formazans and tetrazolium salts

Tetrazolium salts have long been known as heterocyclic organic compounds (i.e. quaternary ammonium compounds) with a significant property of forming water insoluble, highly coloured formazans by reduction. Due to this characteristic property and their low reduction potentials these compounds have been used as reagents for the detection and study of reducing enzyme systems and for the detection and estimation of reducing functions of organic compounds (Altman, 1976). They have also been used in botany as colouring compounds sensitive to UV radiation, to estimate the viability of seeds of agricultural plants, to distinguish between normal and malignant tissues and as analytical reagents to detect O_2^- radical ions . The formation of the coloured formazans can also be utilised for dosimetry of ionising radiation.

The chemical preparation of tetrazolium salts was carried out by the oxidation of the corresponding formazan, which according to Altman (1976), was first prepared by Friese in 1875, but without being aware of the structure of the compound. Von Pechman and Bamberger independently synthesized the colour formazans in 1892 and a year later Von Pechman and Runge oxidized the formazan to form tetrazolium salt (i.e. the triphenyl-tetrazolium-chloride) and confirmed its structure. He and his co-workers prepared at that time a large number of formazans and tetrazolium salts and studied their properties.

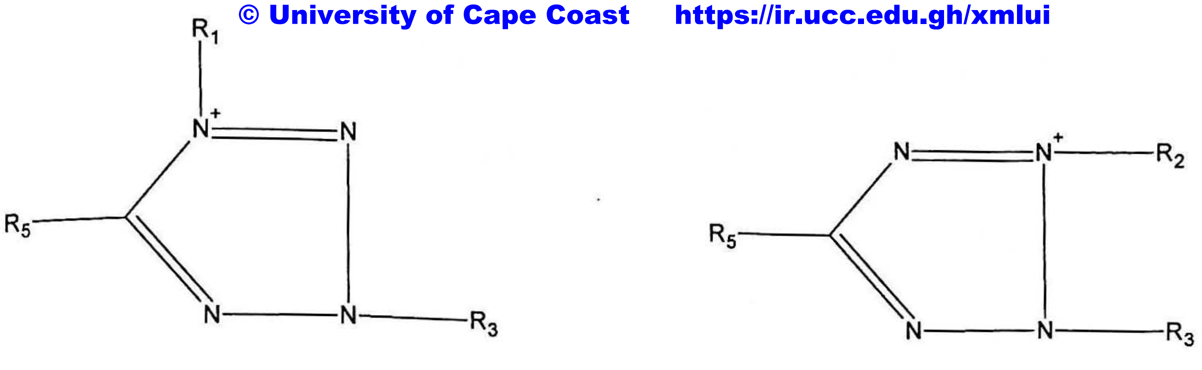
The structure of tetrazolium salts

The tetrazolium salts are quaternary derivatives of the tetrazoles and have the following structure:

(1H) tetrazolium salt (2H) tetrazolium salt

Fig. 1: General Chemical Structure of Tetrazolium salts

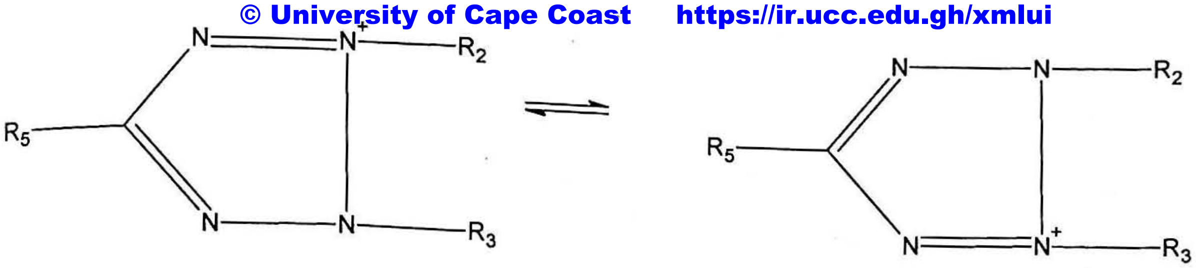
The vast majority of tetrazolium salts, which have been prepared, and all those which have found biological applications belong to the (2H) group. According to Altman (1976) the tetrazolium ring exists as a resonance hybrid of the two extreme forms:

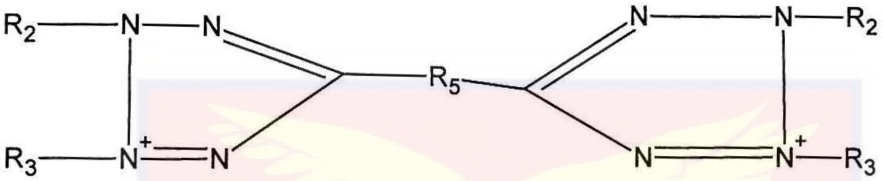


(1H) tetrazolium salt. ↔ (2H) tetrazolium salt.

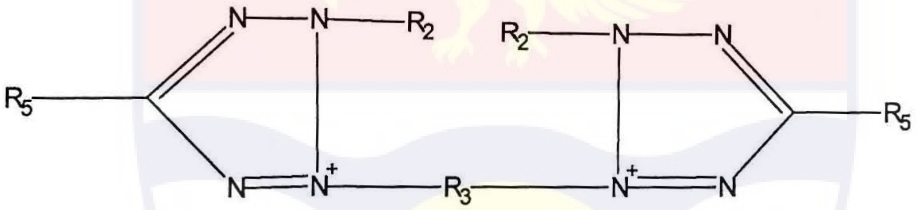
Fig. 2: Structure of Tetrazolium salts showing the resonance hybrid between the H and 2H groups

There are three types of tetrazolium salts, i.e. the monotetrazolium (as explained above), the N-N ditetrazolium and the C-C ditetrazolium salts as shown in Fig. 3. Out of these three types of the salts the monotetrazolium and the N-N ditetrazolium salts are of greater importance due to their ease of preparation and application.





C-C ditetrazolium salt



N-N ditetrazolium salt

Fig. 3: Chemical Structure of the 3 types of Tetrazolium salts

Synthesis and characteristics of tetrazolium salts

Tetrazolium salts are prepared by oxidation of the corresponding formazan. The most practical method of preparation is to react an aldohydrazone with a diazonium hydroxide to give the formazan, and then oxidize it to the tetrazolium salt.

Tetrazolium salts are stable compounds and somewhat soluble in water. Their solutions are colourless or very pale yellow. The reduction of these tetrazolium salts results in a ring opening followed by the production of coloured (e.g. pink, orange-red, red or lilac) compounds known as formazans:

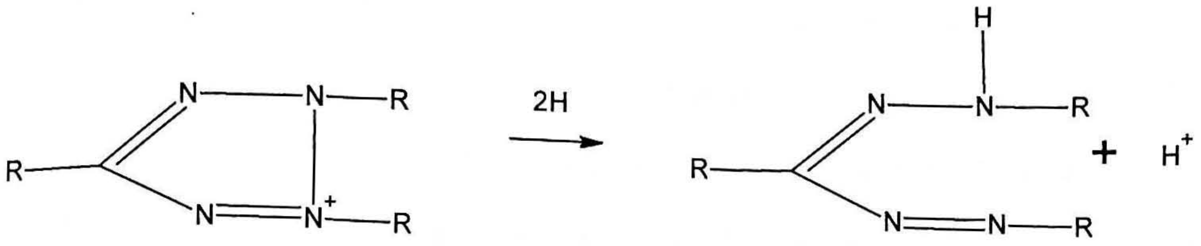


Fig. 4: Reduction process leading to formazan

In systems exposed to ionizing radiation the radiolytic reduction also results in the formation of coloured formazans and this process can be applied in radiation processing for process control by using solutions or solid matrices containing a tetrazolium salt.

Radiation chemistry of tetrazolium salts

A number of investigations have been carried out to study the radiolytic reduction of different tetrazolium compounds in various solvents and solid matrices using both electron pulse radiolysis and steady-state gamma radiolysis.

Radiolysis of liquid systems

The radiolytic reduction of tetrazolium salt is a two-electron process, i.e. the reduction of each tetrazolium molecule needs two reducing species (Pikaev and Kriminskaya, 1998). In alcoholic solutions it was estalbished that these salts are reduced not only by the e^-_s, but also by hydroxyalkyl radicals originating from the radiolysis of the alcohol (e.g. ethanol or isopropanol) (Kriminskaya et al, 1984). While studying the radiolysis of 2,3,5-triphenyl-tetrazolium chloride (TPTC), it was also observed that the reaction of the tetrazolium salt (i.e. cation) with the reducing species leads to the formation of an intermediary product, called tetrazolium (or tetrazolinyl) radical, which then disproportionate giving rise to formazan as the main radiolysis product.

The structure of the tetrazolium radical was confirmed by EPR studies of irradiated frozen solutions of TPTC and TPTC tetrafluoroborate recording two identical EPR spectra (Kriminskaya et al., 1987 and Kriminskaya et al., 1991). In irradiated alcoholic solutions of tetrazolium salts, the tetrazolium radicals are characterized by an intense optical absorption in the visible and UV spectral regions (Pikaev and Kriminskaya, 1998). It was also found that the yield of formazan decreases in the radiolysis of tetrazolium salts when high doses are applied due to further reduction of the formazan to hydrazine (Kriminskaya et al., 1983). This effect is due to further reaction between the formazan formed with the solvated electron and the hydroxyalkyl radicals, if the solution contained alcohol. The yield of formazan was also found to be significantly lower in aerated alcoholic solutions compared to deaerated (e.g. N_2 saturated) solutions. This is explained to be due to the competing oxidation effect of oxygen.

In aqueous or aqueous-alcoholic solutions of tetrazolium salts several authors have found the same basic radiolysis process, i.e. the formation of formazans via a reduction reaction (Pikaev and Kriminskaya, 1998). In deaerated aqueous solution of tetrazolium salts, the formation of precipitates was observed, which can be dissolved in an alcohol or an appropriate organic solvent. The optical absorption spectrum of the dissolved precipitate is however typical of that of the formazan. As a consequence in solutions of aqueous alcohols (especially with higher alcohol concentration) no precipitation was observed. In aqueous solutions the basic radiolysis products of water react with the tetrazolium salts, i.e. the hydrated electron reduces the salt to tetrazolium radicals; the H atoms add to the benzene rings to form H-adducts; the reactions of OH radicals result in OH-adducts. The latter two processes give no formazans, except the reduction process. Higher yield of formazans was observed in alkaline aqueous solutions containing organic compounds (e.g. formate or alcohols), due to the formation of additional reducing species which adds on to the reduction of the tetrazolium radicals. The effect of aeration or deaeration was investigated by Gruenewald (1964), Schmidt-Lorenz (1961) and Pikaev and Kriminskaya (1998) revealing contradictory results which point to the fact that the formazan formation depended on the type of tetrazolium salt investigated. The radiolysis of aqueous nitro-tetrazolium blue (NTB^{2+}) which is a ditetrazolium salt was investigated by Bielski and coworkers (1980) by the stopped-flow and the pulse radiolysis method. In the latter, a formate containing aqueous solution of NTB^{2+}, the tetrazolium radicals form. Their reaction to produce monoformazan was shown to depend strongly on the pH of the solution. In this case the reduction of the NTB^{2+} cation to diformazan is a four-electron process involving the consecutive formation of monotetrazolium radical ($NTB^{+\cdot}$), monoformazan ion (MF^{+}), monoformazan radical ($MF^{\cdot}$) and the final diformazan (DF) product as shown on the reaction scheme below (Fig.5) reveals that while monotetrazolium salts are reduced by a two-electron process to form the formazan, four-electron processes are required to completely reduce the ditetrazolium salts to the diformazan. This assertion was confirmed by Kovacs et al (1999) in their study of NBT under oxidative and reductive conditions.

The radiolysis of 3α-naphthyl-2, 5-diphenyl-2H-tetrazolium chloride also called tetrazolium violet is believed to follow the two-electron reduction process as all other monotetrazolium salts. The mono-tetrazolium salt produces only one formazan, which is formed by the capture of two electrons and one proton (known as a hydride ion, H$^-$) see Fig. 6.

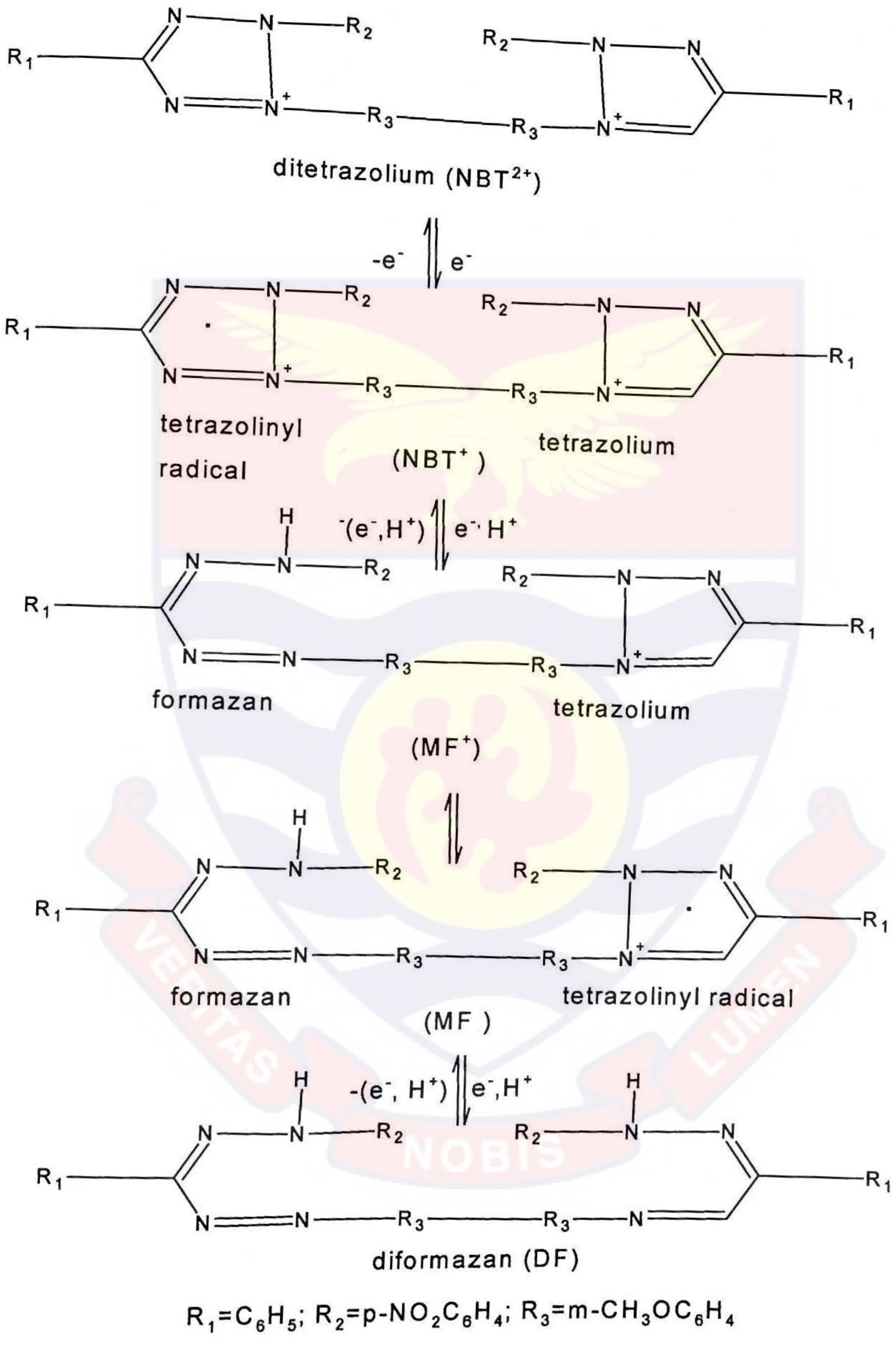
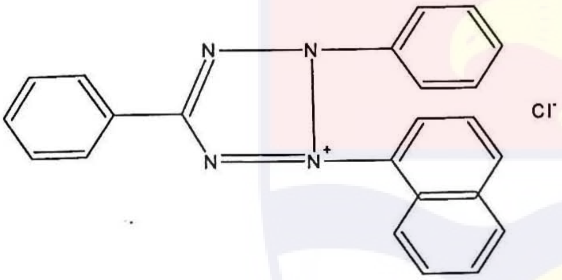


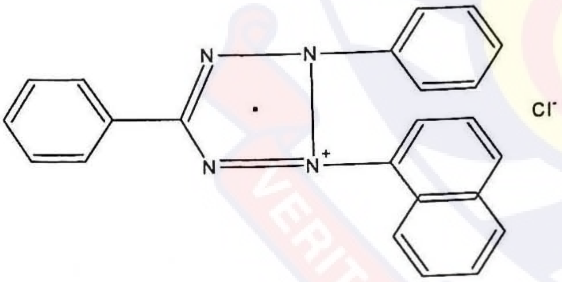
Fig. 5: Reaction scheme of the two electron step reduction of NBT^{2+}

Radiolysis of solid matrices

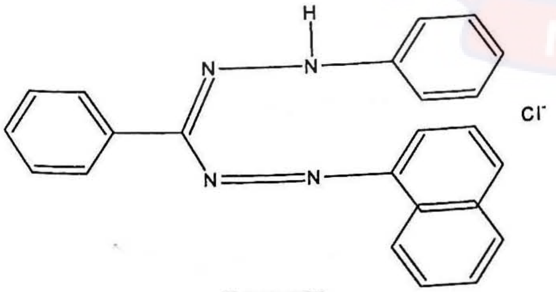
Polymeric films (e.g. polyvinyl alcohol) containing tetrazolium salts (mainly TPTC) have been studied with the aim of using them for dosimetry purposes. The EPR investigations of Kriminskaya et al. (1990) revealed the presence of three paramagnetic species at 77 K, while only one occurred at room temperature, all with reducing properties. At higher temperatures these radicals become mobile and together with electrons can react with tetrazolium salts to form formazans again via a two-electron process.



3α-naphthyl-2,5-diphenyl-2H-tetrazolium chloride (Tetrazolium violet)



Tetrazolinyl radical



Formazan

Fig. 6: Proposed chemistry of the Radiolytic reduction of tetrazolium violet

The application of tetrazolium salts for dosimetry

The basic colour change phenomenon observed during the irradiation of liquid or solid systems of tetrazolium salts, (i.e. from colourless or yellowish to pink, orange, red or lilac due to the formation of formazans), can be used for dosimetry purposes. Different tetrazolium salts have so far been studied from this point of view. One of the most widely studied system is the 2,3,5-triphenyl-tetrazolium chloride, which was investigated both in solutions and solid matrices. Gierlach and Krebs (1949) observed the appearance of red colour upon UV light exposure, as well as α- or X-ray radiation of its aqueous solutions and gelatine emulsions. On this basis, the salt was suggested for use in radiology and radiobiology to make three-dimensional dose distribution images upon X-ray treatment. It was also shown that the concentration of the formazan produced depends linearly on the dose up to about 12 MGy. Studying the influence of parameters like pH, concentration, aeration or de-aeration and dose rate on the formazan formation (G(F)), it was found, that in aerated solution the formazan formation does not depend on the pH between 5 and 8. At higher pH, the G(F) increases, while at lower pH, the G(F) decreases. It was also shown that the G(F) value is about twice as much in de-aerated solutions as in aerated ones, while in O_2 saturated solutions the formazan yield is about 2.7 times lower compared to the yield in aerated solutions. It was established that doses up to 36 kGy can be measured with such solutions as found. The possibility of measuring absorbed doses between 1 and 16 kGy was shown by using alcoholic solutions of 0.045 mol dm^{-3} TPTC, showing a linear response between dose and absorbance at 480 nm where the triphenyl formazan product formed (Kovacs et al, 1995). In conclusion it was noted, that the advantage of using this solution is, that under controlled conditions a relatively stable system can be maintained.

In order to look for a routine evaluation method for irradiated alanine powder, instead of the expensive ESR analysis, the use of aqueous TPTC solution was investigated. By dissolving the irradiated alanine powder in the TPTC solution, the appearance of the absorbance of the pink-coloured formazan was observed at 401 and 487 nm. This readout method can be used in the 2-200 kGy dose range (Ebraheem S. et al, 1999).

At higher doses the formazan formed earlier starts to decompose resulting in nonlinear dose dependence. In aqueous solutions the formazan yield was found to decrease with decreasing TPTC salt concentration. The temperature coefficient of this yield was found + 0.8 % per °C in the range of 0 -30 °C, while it gets significantly bigger up to 60 °C. It was also observed, that daylight and bright sunlight lead to the slow formation of formazan. Therefore the solutions must be stored in dark and five days dark storage was shown not to affect the unirradiated and irradiated solutions. Kovacs et al. (1995) studied the pulse radiolysis of the same TPTC salt and confirmed the bimolecular formation of the formazan product under reducing conditions. A poly (vinyl alcohol) based TPTC film was also produced and tested. A measurable response in the 1 - 100 kGy dose range was observed by evaluating the irradiated 50 μm thick dosimeters at 493 nm. Since the film was found to be sensitive to such environmental conditions as irradiation temperature, light and humidity, its careful characterization was suggested for process control dosimetry.

Tetrazolium salt contained in polymeric films were also prepared and studied for dosimetry purposes even earlier. More than half a century ago the Kodak Pathe Company developed a gelatine film containing TPTC suitable for measuring doses up to a few tens of kGy. Other matrices like poly (vinyl acetate), poly (vinyl alcohol) and polyvinylpyrrolidone were also studied for dosimetry purposes. The most thoroughly investigated tetrazolium film TPTC was prepared in poly (vinyl alcohol). These films can be used for dose measurements in the range of about 0.5 - 100 kGy. These films are affected by light and by temperature. The temperature coefficient of the film was found to be about + 0.46 % per °C, while light effects can be avoided by storage in dark. The TPTC containing poly (vinyl acetate) based films were found to be suitable for dose determination between 5 and 50 kGy and can also be used to obtain radiographic images.

CHAPTER 4

THEORY

Theoretical analysis

In this chapter the theory of the pulse radiolysis for the dynamic studies to observe the kinetic behaviour of the intermediary species formed in the solutions studied are presented together with the steady state and dosimetry investigations.

Electron beam accelerator and the pulse radiolysis setup with kinetic spectrophotometric detection

A pulse of electrons accelerated in the linear electron accelerator (LINAC,) as shown Fig. 7 and 8 with electron energy ~ 4 MeV reaches the sample placed in a special quartz cell inducing radiolysis processes. A simultaneous blast of analyzing white light goes through the cell, where it is partially absorbed by the radiolytic products formed as a result of the ionizing radiation interaction with the sample under investigation. The light is then "trimmed" to the selected UV-VIS wavelength on a monochromator and converted to electric signal by the photomultiplier. The signal is then amplified and analogue to digital conversion is applied by the digital oscilloscope unit. Time courses of signal changes in the time scale ranging from several nanoseconds to seconds after the electron pulse are recorded by a PC unit and recalculated to absorbance changes.

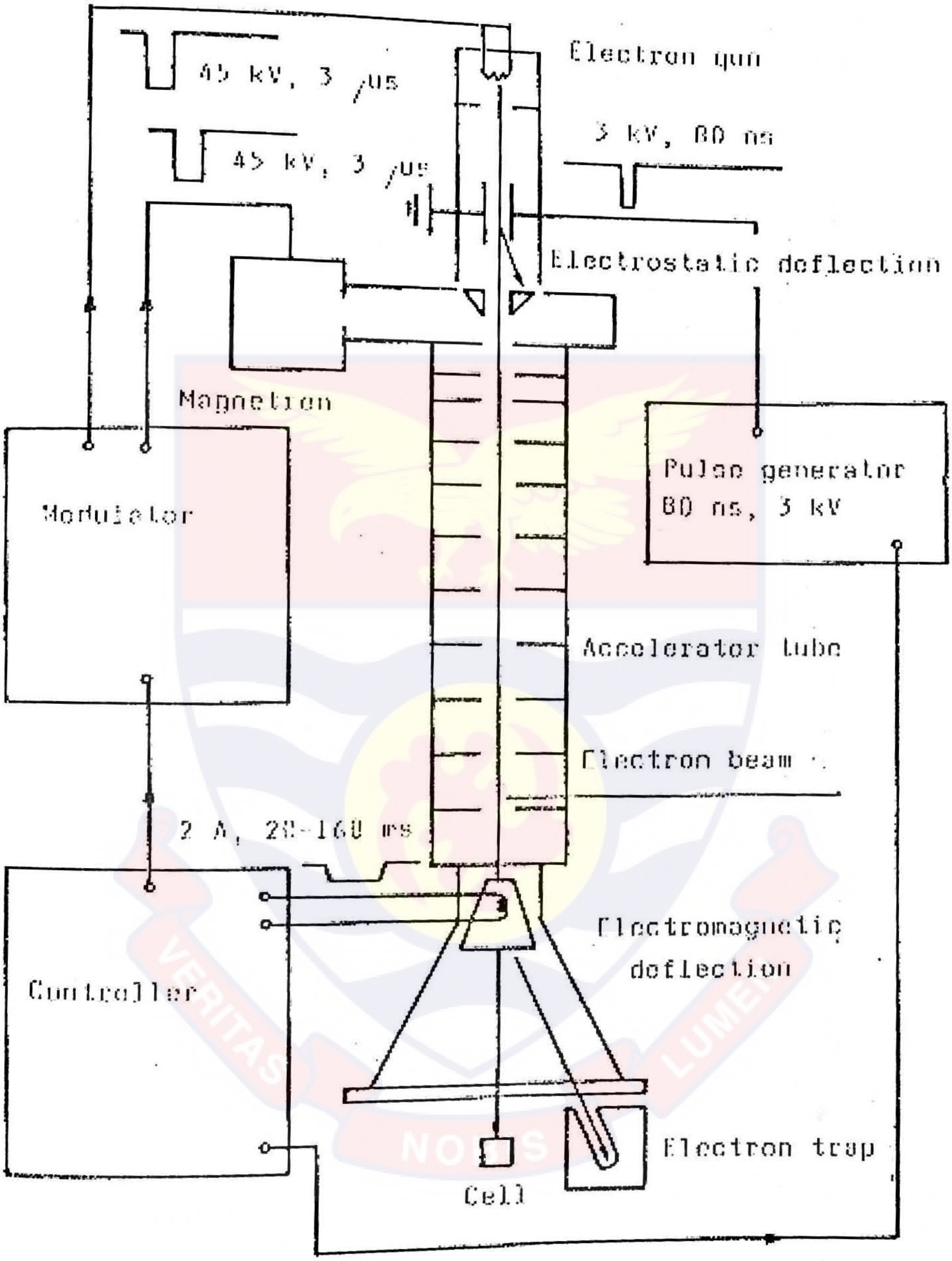
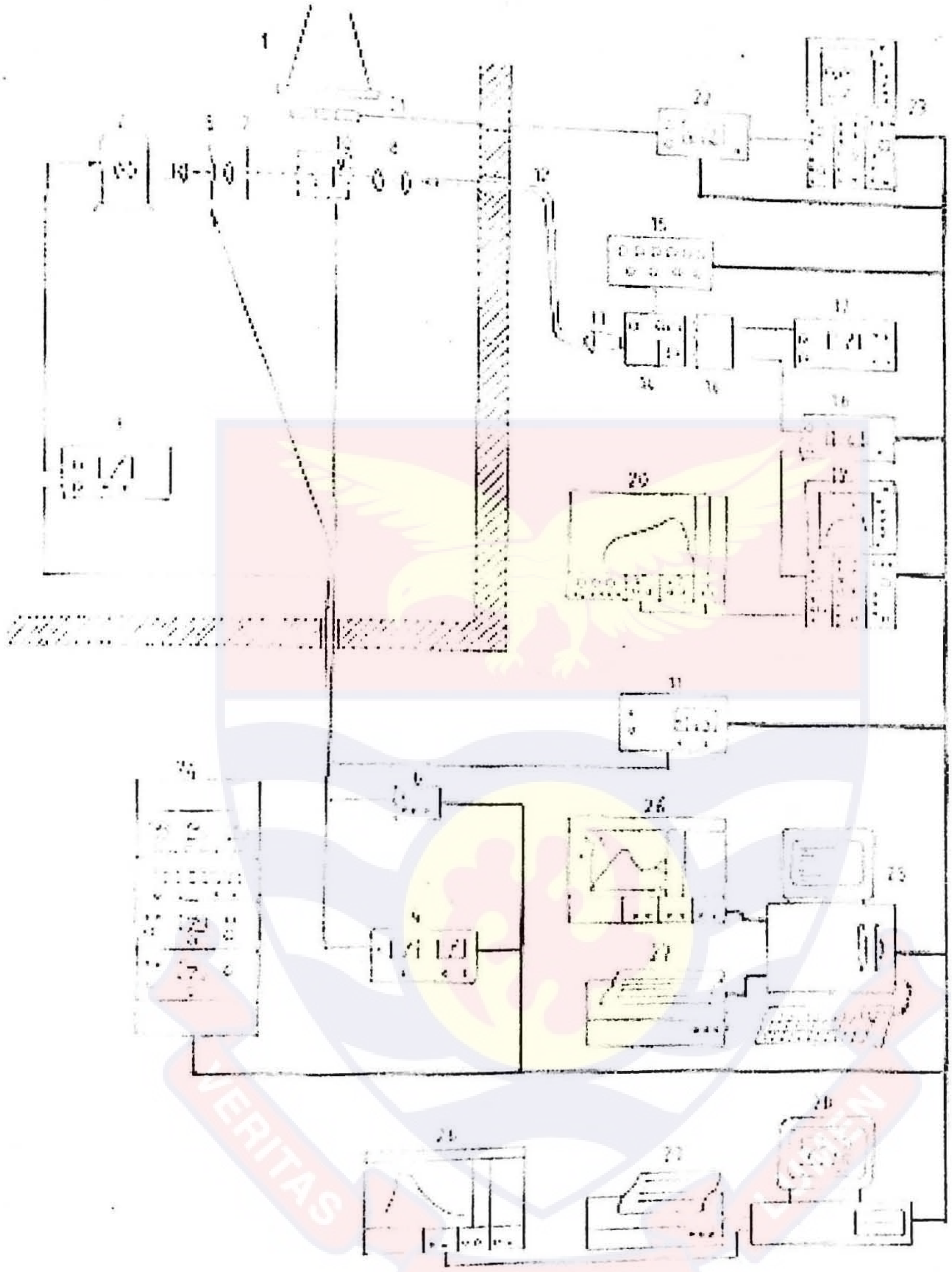


Fig. 7: The LPR-4 linear electron accelerator



1.Linac exit port; 2. Xe arc lamp; 3. Lamp power supply; 4. Lamp pulsing unit; 5. Shutter; 6. Shutter control; 7. Iris; 8. Lenses; 9. Cell; 10. Thermostat; 11. Thermostat control; 12. Loight guide cable; 13. Focussing lens assembly; 14. Monochromator; 15. Monochromator control; 16. Photodetector; 17. Photodetector supply; 18. Backing off unit; 19. Digital Oscilloscope; 20. X-Y recorder; 21. Dose Monitor; 22. Dose monitor display; 23. Oscilloscope for setting the dose monitor; 24. Linac control unit; 25. Cromemca Computer; 26. Plotter; 27. Printer; 28. Varyter Computer

Fig. 8: Scheme of the pulse radiolysis set-up

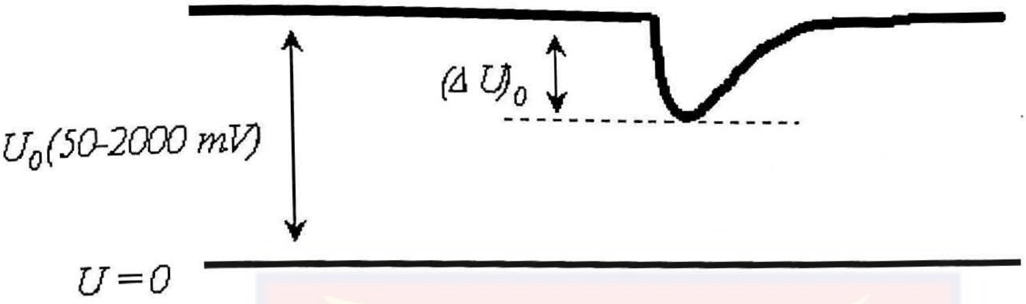


Fig. 9: Display of absorption signal on oscilloscope due to radiolysis products.

The absorbance (A) of the light of intensity I_o in the sample is given by the relation:

$$A = \log(I_0 / I) = \log[I_0 /(I_0 - \Delta I) \quad 4.1$$

After absorption, the emergent intensity incident "I" on the photomultiplier is converted into electrical signal (Fig. 9) which reaches the oscilloscope and computer assembly. Equation 4.1 may therefore be expressed as:

$$\cong \log[i_0 /(i_0 - \Delta i)]$$

$$= \log[U_0 / U_0 - \Delta U) \quad 4.2$$

Where i_o and i are currents associated with the incident and transmitted light which give rise their respective voltages U_o and U established across a resistor in the oscilloscope.

However by (kinetic) spectrophotometry the time-dependent absorbance A of the intermediates is given by Lambert-Beer law as;

$$A = \varepsilon_{\lambda} c l \qquad 4.3$$

where ε_{λ} is the molar extension coefficient of the studied species in the solution whose concentration is "c" for the wavelength λ and l is the optical path length in the measuring cell. The time-dependence of concentration for first order decay is given as (Foldiak, G., et al., 1988)

$$c = c_{o} e^{-kt} \qquad 4.4$$

where c_0 is the initial concentration and k is the reaction constant. By substitution the equations are simplified as follows:

$$A = A_{o} e^{-kt} \qquad 4.5$$

Hence the measure of absorbance as registered on the computer or oscilloscope is proportional to the measure of concentration.

Gamma irradiators and steady state radiolysis

The radiolysis products for the gamma irradiation shows no intermediary products or species but the final products of the irradiation called the formazan. In effect, gamma irradiation leads to steady state radiolysis while the electron pulse leads to the dynamic studies or investigation of the intermediary radiolysis products.

The Lamberts-Beer law therefore similarly applies when the light passes through the cell with the solution of TV in a spectrophotometer. In such a steady state investigation, equation 4.3 is applicable and the absorbance is dependent on the concentration of the formazan formed in the solution which in effect is proportional to the dose given to the TV solution.

CHAPTER 5

EXPERIMENTAL METHODS

Experimental Methods

The experimental work used to investigate the dosimetry characteristics of 2, 5-dipheny-3-(1-naphthyl)-2H-tetrazolinum Chloride and in comparison with the Fricke and Ethanolchlorobenzene dosimetry systems are presented in this chapter.

Facilities and methods used

In this study different facilities and methods have been used to determine the characteristics of tetrazolium violet (TV) for radiation processing dosimetry. These include

(i) irradiation facilities for steady state (i.e. gamma radiolysis) and dynamic state (i.e. pulse radiolysis) studies

(ii) preparations of solutions and films

(iii) studies of influence parameters like irradiation and storage temperature, relative humidity, dose rate, etc

(iv) comparative response studies with known dosimetry systems based on the optical absorbance of the solutions and films using UV spectrophotometric analysis.

The gamma irradiation and linac electron beam facilities used to study the responses of the tetrazolium violet to gamma and electron beam irradiations are discussed below. The effect of TV concentration, irradiation of TV solutions under oxidizing and reducing conditions, at high and low pH among others, enabled investigations to determine the effect of influence parameters on the responses of the various TV systems studied. The response of TV systems under industrial conditions was undertaken to ascertain the suitability of the TV for radiation processing dosimetry.

Gamma irradiation facilities

The gamma irradiations were carried out with two ^{60}Co facilities, i.e. the Multi-purpose SLL-04 Gamma Irradiation Facility (1.85 PBq, March 1994) at the Ghana Atomic Energy Commission, the Pilot Scale SSL-01 Gamma Irradiation Facility (3.7 PBq, June 2002) of the Institute of Isotopes, Hungary and the JS-6700 type gamma irradiation facility (12.2 PBq) of Dispom Edicor Rt at Debrecen, Hungary.

In all cases irradiation of samples were performed in a polystyrene holder (wall thickness: 5 mm, to ensure electron equilibrium), in the centre of the sample chamber as shown in Fig. 10, where the dose rates had been determined by Fricke or ethanol-chlorobenzene dosimetry systems for the facility in Ghana with maximum dose rate of 2.4 kGy/h and Hungarian facility also with maximum dose rate of 18 kGy/h. The response of the ECB transfer standard dosimeter was used traceable to the alanine dosimeter at the High Dose Dosimetry Laboratory of RisØ National Laboratory.

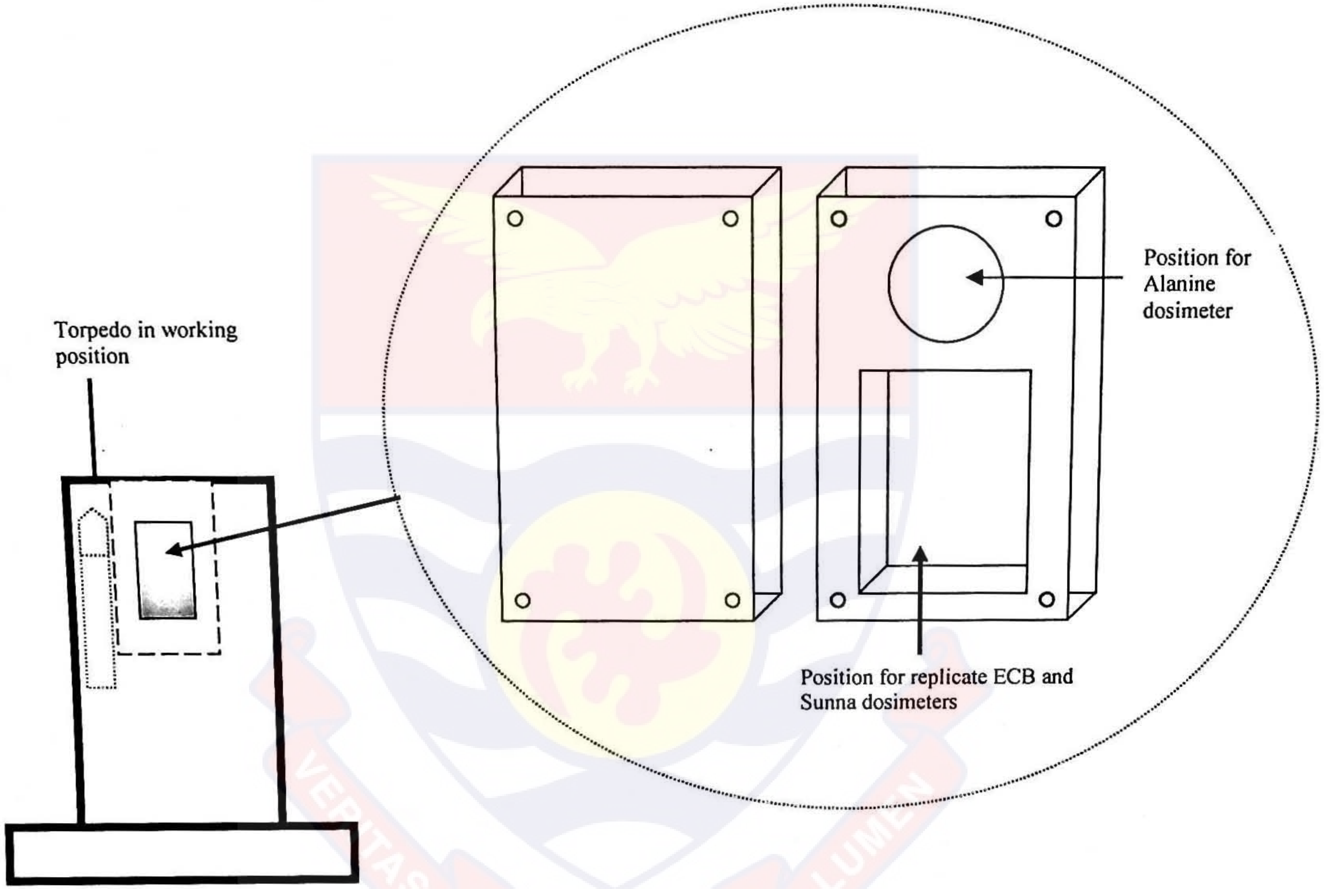


Fig. 10: Diagram showing position of samples during irradiations in gamma facilities

Electron irradiation facilities

Two types of electron beam irradiation facilities were also used; one for the pulse radiolysis studies of the tetrazolium violet solutions and the other one for routine industrial type irradiations.

Electron pulse radiolysis system

The electron pulse radiolysis investigations were carried out using the LPR-4 linear electron accelerator (Tesla Vuvet, Czech Republic) of the Institute of Isotopes, Hungary, as shown in Fig. 7 and 8. The accelerator produces electrons with an average energy between 3 and 5 MeV working in a pulsed mode with 200 mA peak current. The electron pulses are produced in two basic modes of operation, i.e. either single pulses are produced by an external trigger or continuous train of pulses produced at a frequency of 6.25 Hz, 12.5 Hz, 25 Hz or 50 Hz. The usual pulse length is 2.6 μs, but shorter pulses using an electrostatic deflection system can also be produced.

The computer controlled optical detection system used for the electron pulse radiolysis investigations is a kinetic spectrophotometer (Applied Photophysics, type K 347), suitable both for absorption and emission measurements as described in Chapter 4 The time dependent concentration of unstable, optically absorbing species produced by irradiation is followed by kinetic spectrophotometry. Using this measurement technique the reference light level μ_o (i.e. 50 ~ 2000 mV) is measured through the sample before it is irradiated. The high sensitivity of the kinetic spectrophotometry method enables absorbance changes ~ ΔA (i.e. equivalent to Δμ) of less than 1 % in the transmitted light level to be measured with suitable accuracy. The other advantage of the method is its fast response time.

One part of the measuring set-up is located in the irradiation room, while the other part (i.e. readout section) is in the control room (Fig. 7 and 8). The section of the LINAC in the irradiation room consists of the light source (i.e. a high pressure pulsed Xe lamp, 250 W) for the illumination of the samples, the lens system, the shutter (i.e. which helps to prevent the heating and the photolysis of the sample) and the measuring cell. The lenses and cells are made of high quality synthetic quartz (Suprasil) to ensure radiation resistance. The other part of the set-up located outside of the irradiation room includes the analysing light (wavelength range of 300 - 800 nm and 400 - 1000 nm), which is transmitted into the monochromator through glass light guides and then through the photomultiplier into the Iwatsu TS 8123 oscilloscope. The oscilloscope system digitalizes the analogue signal, stores and transmits to the computer system for data acquisition and processing (e.g. for kinetic analysis) (Foldiak G. et al, 1988). The experimental set-up of the pulse radiolysis system is shown in Fig. 7 and 8.

Other electron irradiation facilities

The tetrazolium violet film samples for calibration and comparison with other dosimeters were carried out using the 7 MeV linac electron beam accelerator in Budapest, Hungary.

Chemicals

The tetrazolium violet (3α-naphthyl-2,5-diphenyl-2H-tetrazolium chloride, $C_{23}H_{17}ClN_4$, MW: 817.6) was obtained from Aldrich and used without further purification. The aqueous and aqueous-ethanolic TV solutions were made using double distilled water and absolute ethanol (Merck, puriss). The pH of the solutions was set with HCl for low pH and NaOH for high pH both from Reanal. The solutions were irradiated in sealed glass ampoules. For the deaerated pulse radiolysis experiments, the aqueous solutions were bubbled with N_2 or N_2O. The tert-butanol used for some of the solutions was obtained from Reanal. For the preparation of the films, 5% aqueous polyvinyl alcohol from olyscience Inc was used.

Preparation of tetrazolium violet solutions

The solutions were prepared by dissolving the appropriate quantities of tetrazolium violet in double distilled water and where other solvents like ethanol or tert-butanol were involved, the appropriate quantities were also added. Solutions of high pH were obtained by the addition of NaOH whilst low pH were prepared by the addition of HCl All but one of the solutions investigated were air saturated by just covering the ampoules with aluminium foils and not by flame sealing. In the case of the N_2 saturation or dearations the ampoules were filled first with the solution and bubbled with N_2 gas for about 20 minutes to remove oxygen and then flame sealed immediately.

TV solutions were gamma irradiated in 10 ml glass ampoules. The isotropic assembly of Co-60 facilities were used to deliver doses from 0.5 to 50 kGy.The absorbance spectra were taken immediately after the irradiations, but to study the "fading effect" on the response of the TV solutions the absorbance spectra of the samples were measured for 7 days after the irradiation.

Tetrazolium violet in water

To prepare 1 mM TV solution, 77 mg of TV was dissolved in 200 ml of double distilled water. By direct proportions 0.5 and 2 mM solutions were also prepared for investigations. The pH of the 1mM solution was determined to be 5.6. The high pH obtained by the addition of NaOH was made to be between 10.4 and 10.8, whilst the acidic solutions had pH between 3.0 and 3.3 by the addition of HCl. The 0.5 mM and 2 mM solutions were also prepared in the pH range between 6.13 and 11.57.

Tetrazolium violet of 50:50 % water/ethanol solutions

In the preparation of aqueous-ethanol solutions of TV, 77 mg of TV was dissolved in mixed solution of 100 ml double distilled water and 100 ml of ethanol. The pH was measured to be 6.32 and irradiations were carried out under air saturation.

Tetrazolium violet solution with 0.5 M tert-butanol

TV solutions containing tert-butanol were prepared by adding 500 ml of 1mM TV solution to a solution containing 96.2, and 6 ml (i.e. 0.5 M) of tert-butanol in 500 ml double distilled water. The pH of this solution was 6.9, while solutions of low pH = 3.4 and of high pH = 10.4 were also prepared and studied. Again air saturated solutions were irradiated.

Preparation of radiochromic dye films of tetrazolium Violet

The TV containing radiochromic dye films were prepared by first dissolving the appropriate quantity as described above and the pH set as required for the given solution. A liquid solution of the film is then prepared by dissolving 6g of the 5 % aqueous polyvinyl alcohol (PVA, Polysciences Inc., MW: 108.000) in double distilled water and when a clear or turbid solution was obtained, the already prepared TV solution was added. The mixture was then magnetically stirred for at least 30 minutes and poured onto a glass plate to allow for drying.

Absorbance measurements and physical observation of samples

For the solutions steady state gamma irradiation investigations were carried out in air saturated solutions in 10 ml glass ampoules covered with Al foils. The irradiations were performed in an isotropic assembly of Co-60 sources in an annular arrangement either at the gamma facility of the Institute of Isotopes (Budapest, Hungary; absorbed dose rate of 15 kGy/h as established by ECB calibration dosimetry) or at the gamma irradiation facility of the Radiation Technology Center (Accra, Ghana; absorbed dose rate of 1 kGy/h as established by Fricke dosimetry). Solutions were given absorbed doses from 0.25 to 75 kGy and the optical absorbance values were measured in the wavelength range of 375 - 800 nm using the Jasco V550 or between 400 and 700 nm with the Genesys 5 models of UV-VIS spectrophotometers. The solutions irradiated to higher doses (> 20 kGy) were diluted 10 times after irradiation with unirradiated solution for the spectrophotometric measurements. The optical absorption spectra were taken immediately after the irradiations, but to study the "fading effect", the spectra of the samples were repeatedly measured daily for a week after the irradiations.

The colour change of each sample before and after irradiation was noted. In those cases when precipitates were formed, the colour and nature of the irradiated solutions were also noted.

In the case of the films, gamma irradiations were carried out in a perspex phantom at the Institute of Isotopes Ltd. Co. (Budapest, Hungary) using the SSL-01 type ^{60}Co irradiation facility (nominal activity: 3 PBq, dose rate: 12 kGy h^{-1}) and at the gamma irradiation facility of the Radiation Technology Center (Accra, Ghana; nominal activity: 3.7 PBq, dose rate: 1 kGy h^{-1}). Electron irradiations were carried out at the Institute of Isotopes (Budapest, Hungary) using the 4 MeV LPR-4 type linear electron accelerator.

The optical absorption spectra and the absorbance values were measured with a Jasco UV-VIS 550 type or a Genesys-5 UV-VIS spectrophotometer.

Dosimetry system used during the investigations

Different dosimetry systems were used to determine the dose rate at the different gamma irradiation facilities and for measuring the absorbed dose during the characterization of the TV solutions and films. The response of the TV solutions or films was therefore compared with that of established dosimetry systems.

During the industrial scale electron irradiations, the TV film samples were irradiated in polystyrene phantoms of the same size as that of the polystyrene calorimeters used for the field calibration. In order to give the same dose to the film samples as with the calorimeters they were irradiated on the conveyor in rapid succession, close to each other using scanned e-beam.

The fricke dosimetry system

The Fricke solution was used as suggested by the ASTM (IAEA, 1972).The aerated solution was prepared by dissolving ferrous ammonium sulphate $(NH_4)_2Fe(SO_4)_2.6H_2O$, 1 mM) and sodium chloride (NaCl, 1 mM) (both from Reanal, puriss) in 0.4 M sulphuric acid (H_2SO_4) solution made of double distilled water.

The ethanol-chlorobenzene dosimetry system

The ethanol-monochlorobenzene dosimeter solution was prepared as described in the ASTM Standard No. 1538 (2000) by mixing 24 % by volume of monochlorobenzene (Merck-Schuhardt, analytical grade) with 71.92 volume % of absolute ethanol (Reanal) and then adding 4 volume % of double distilled water and 0.04 volume % each of acetone and benzene to the solution.

The potassium cyanide system

The dose per pulse value during the pulse radiolysis investigations was determined by using 10^{-2} M air saturated KSCN solution (Foldiak G. et al, 1988).

Analytical methods

The irradiated Fricke solution, TV solutions and films were evaluated with UV-VIS spectrophotometry using Jasco 550 or Genesys-5 Spectronic spectrophotometers.

The wavelength calibrations were carried out with a standard holmium oxide glass filter, while the absorbance scale was checked with a standard Pye Unicam absorbance filter set.

The irradiated ECB dosimeters were measured by the oscillometric reader (model Radelkis OK-302) according to ASTM Standard No. 1538 (2000).

Response of TV films to temperature and relative humidity Irradiation temperature

Irradiations at constant temperature were carried out at the SSL-01 gamma facility using a temperature controller unit, which can stabilize the irradiation temperature in the range of 10 – 60 °C with an uncertainty of +/- 1 °C.

Effect of humidity on the performance of the film

Humidity studies on the performance of the films were carried out during gamma irradiation in the 12-75 % relative humidity range. The humidity values were achieved by using the following saturated salt solutions: LiCl (12 % relative humidity), $MgCl_2$ x 6 H_2O (34 %), $Mg(NO_3)_2$ x 6 H_2O (55 %) and NaCl (75 %).

The films containing 1 and 10 mM TV concentrations were stored in desiccators for 3 – 6 days before irradiation. The absorbance of the irradiated films dried before irradiation, were measured and compared with the effect of humidity on the TV films at the established humidity environment.

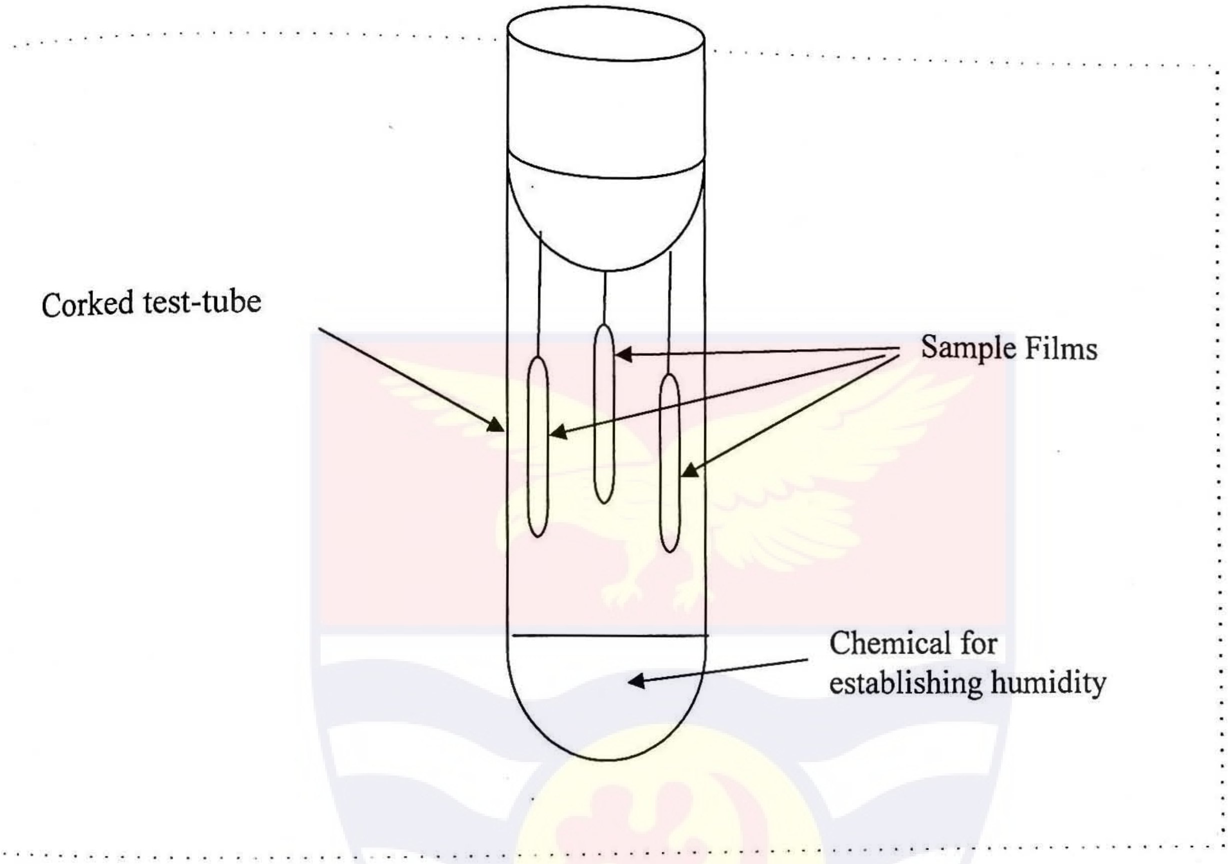


Fig. 11: Set up for humidity investigations

Calibration of the TV film in industrial irradiation facilities

In order to investigate the applicability of the TV films for radiation processing dosimetry, their performance in industrial gamma and electron beam irradiation facilities was investigated. The films were irradiated in polystyrene calibration phantoms together with ethanol-monochlorobenzene transfer standard dosimeter solution for gamma irradiation and with polystyrene calorimeter in the case of electron accelerator.

CHAPTER 6

RESULTS

esults

In order to study the potential applicability of the tetrazolium violet (TV) for osimetry purposes the basic radiation chemical processes in the irradiated aqueous and queous - alcoholic TV solutions were investigated using both electron pulse radiolysis .e. dynamic state) and gamma radiolysis (i.e. steady state) experiments. On the basis of ese results the dosimetry characterization of the solutions was performed. Finally a olyvinylalcohol based TV containing radiochromic dye film was prepared, characterized nd tested for routine dosimetry applications in radiation processing.

lectron pulse radiolysis investigations

The understanding of the primary chemical changes, occurring with the teraction of high energy radiation and liquid, solid or gaseous systems, is due to a gnificant extent on the availability of the electron pulse radiolysis technique, since most f its applications depend on the reactions of ions, atoms, free radicals and excited states. he reason is that these species or states form very quickly on the absorption of the diation. In dilute solutions these primary radiolysis species almost entirely originate om the solvent which then react with the solute leading to the final radiolysis products. o follow oxidation or reduction processes it is necessary to simplify the system under udy by selecting the presence of oxidizing or reducing species resulting in such rocesses, respectively, with the solute.

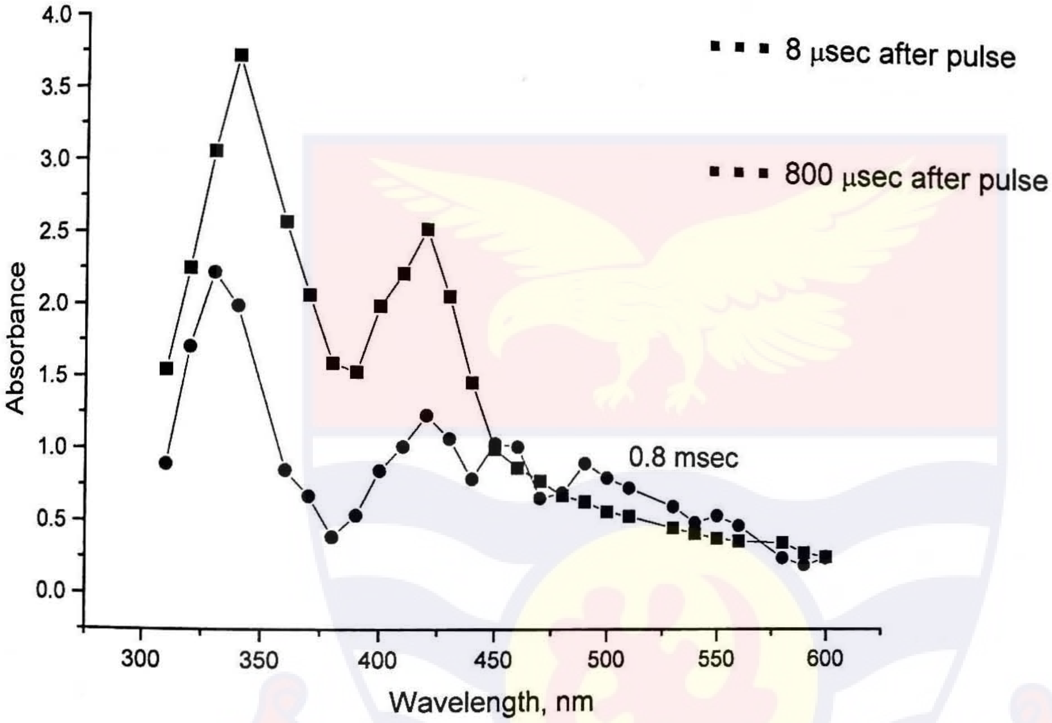
The major reactive species available for reaction with solutes in aqueous solutions re the OH radical (oxidizing agent, G = 2.7), the solvated electron, e_{aq}^- (reducing agent, ; = 2.7) and the H atom (reducing agent, G = 0.6). In acid solutions e_{aq}^- is quickly ransformed to H atom (G = 3.3). These species can be produced in a nanosecond using ulsed electron beam.

The radiolytic reactions of the monotetrazolium violet were studied by pulse adiolysis technique in aqueous solution under reducing and oxidizing conditions with the im of clarifying the early radiation chemical processes taking place in these systems.

adiolysis of TV under reducing conditions

In order to study the aqueous tetrazolium violet system under reducing conditions e oxidizing OH radicals is eliminated from the solution by N_2 saturation and addition of ert-butanol, which also reacts with the OH radical resulting in the unreactive tert-butanol adical. Thus the solvated electron and H atom as reducing reactive species are the only ee reactive species present in the solution together with the tert-butanol radical which as been proved to be rather inactive in reaction with tetrazolium salts. The radiolytic eactions in the 0.1 mmol dm^{-3} TV containing solutions were investigated both in neutral pH = 5.7; pH = 6.7) and in alkaline (pH = 10.8) solutions.

The absorption spectrum - taken 8 μs after the electron pulse in N_2 saturated tert-utanol containing solution pH = 5.7 solution - shows a strong absorption in the 300 nm – 00 nm region with a maximum at 340 nm and a smaller absorption peak at 420 nm ollowed by a decreasing absorption up to about 600 nm (Fig. 12). On a longer time cale, i.e. 0.8 ms after the electron pulse, the absorption at 340 nm and 420 nm gets ignificantly smaller, whilst the absorption observed 8 μs after the pulse in the 450 - 580 m region become rather more pronounced.

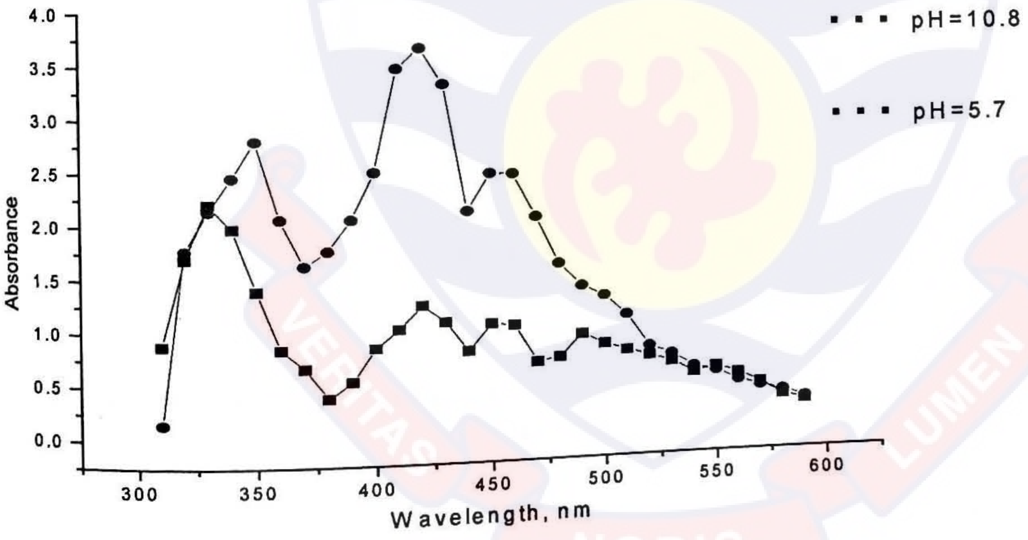


g. 12: Optical absorption spectra in N_2 saturated aqueous solutions of 0.1 mmol n^{-3} of TV containing tert-butanol taken 8 μs and 0.8 ms after the 2.6 μs electron lse (pH = 5.7)

In solutions at pH = 6.7 of the same composition similar absorption spectrum – th a little shift of the position of the two absorption peaks - was observed immediately er the electron pulse. More pronounced decrease of these two absorption peaks was, wever, observed on a longer (ms) time scale.

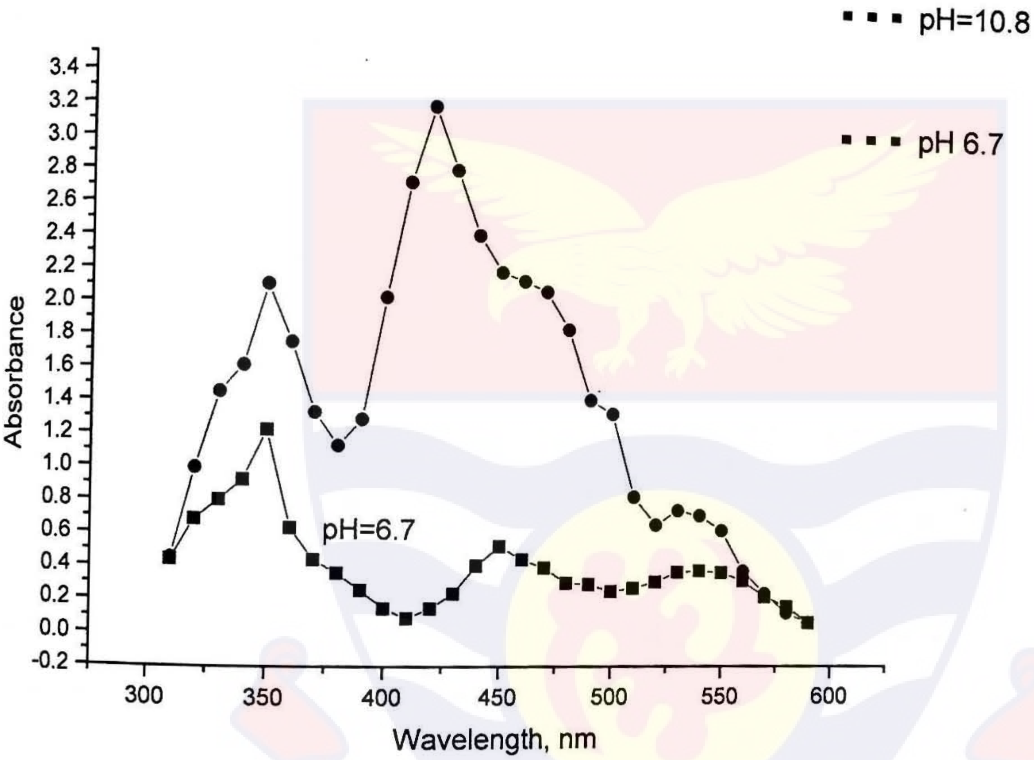
In alkaline solutions (Fig. 13) similar absorption bands like in acidic and neutral utions were observed 7 µs after the electron pulse with maxima at 350 nm and 420 nm. s important to note, however, that with increasing time (i.e. 0.8 ms after the electron se) the decrease of the absorption at 420 nm is much smaller than in the previous es, while the absorption at around 450 nm gets more significant.

When comparing the observations on ms time scale in neutral and alkaline utions similar absorption spectra were found, but significant difference could be seen th in the absorptions as well as in their ratios measured at 420 nm and in the 450 – 580 region, respectively. Much stronger absorption was observed in alkaline solutions an in neutral solution (Fig. 13).



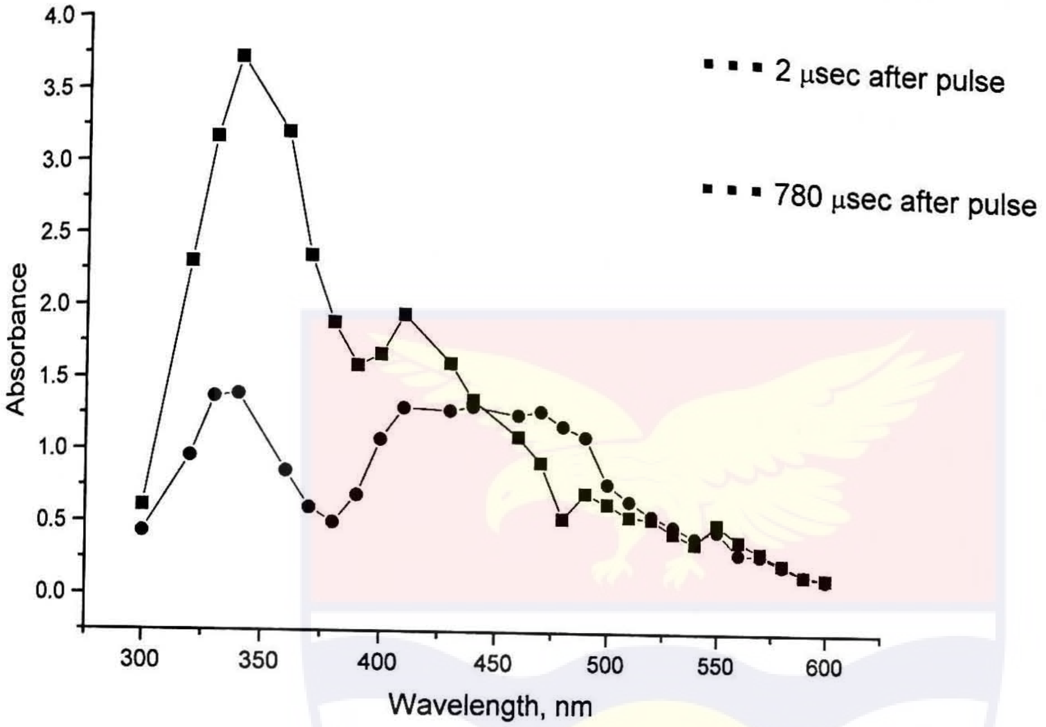
g. 13: Optical absorption spectra in neutral and alkaline N_2 saturated aqueous lutions of 0.1 mmol dm^{-3} of TV containing tert-butanol taken 0.77 ms after the 2.6 electron pulse.

Similar differences were found when the absorption spectra measured in neutral ıd alkaline solutions were compared at1.8 ms after the electron pulse (Fig. 14).



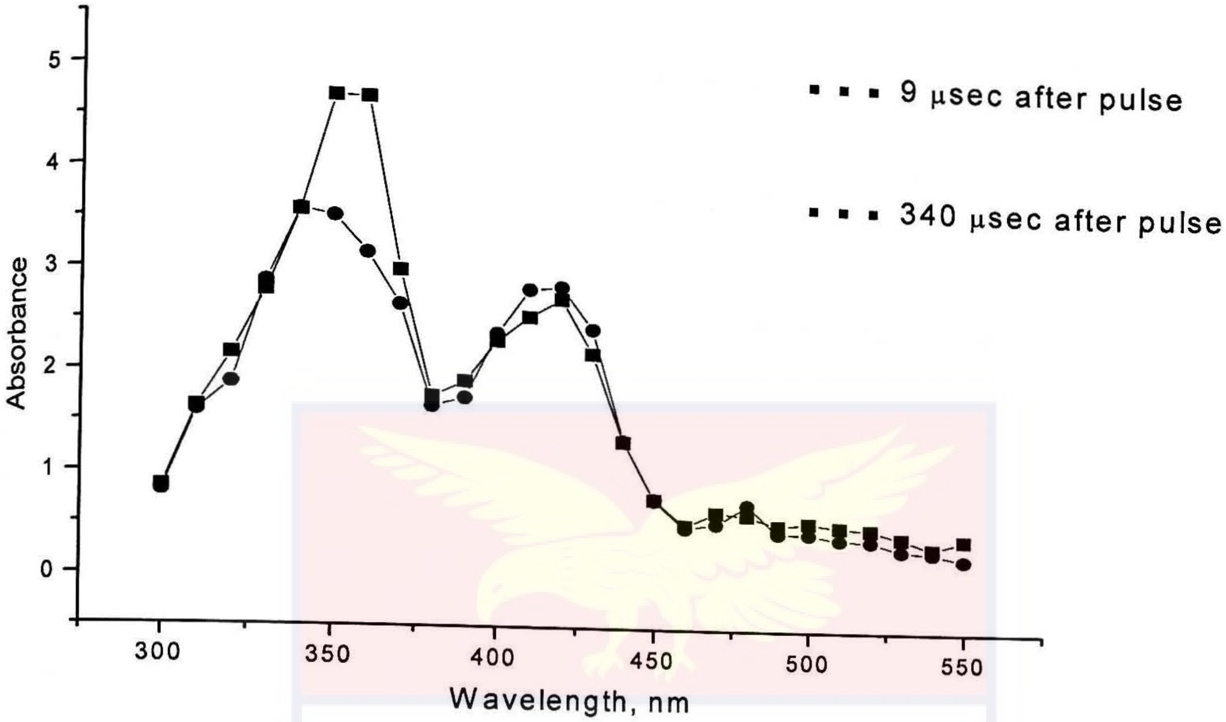
g. 14: Optical absorption spectra in neutral and alkaline N_2 saturated aqueous utions of 0.1 mmol dm^{-3} of TV containing tert-butanol taken 1.8 ms after the 2.6 electron pulse

In acidic N_2 saturated solutions (pH = 3.2) not containing tert-butanol, (Fig. 15) absorption shows a significant decay on the longer time scale of the absorption at 350 a "shoulder" at 410 nm , although its decrease is much smaller on the ms time scale s well as with the "build-up" of the absorption in the 450 nm – 550 nm region (Fig. 15).



g. 15: Optical absorption spectra in N_2 saturated aqueous solutions (pH = 3.3) of 1 mmol dm^{-3} of TV taken 2 μs and 0.78 ms after the electron pulse

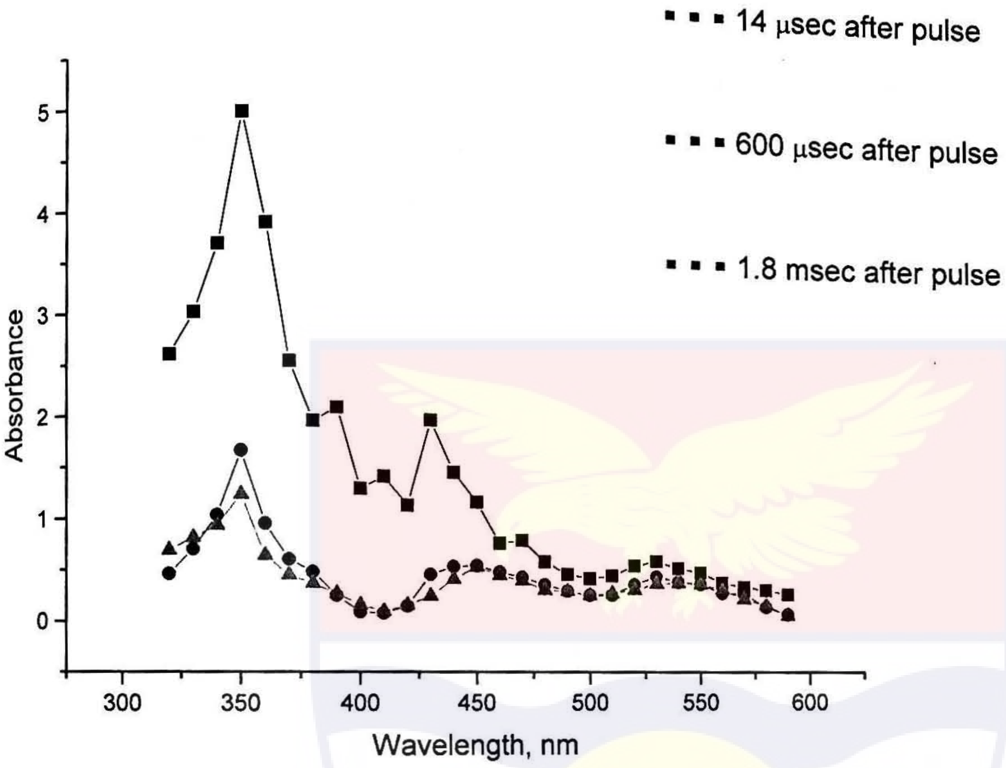
Investigations were also been performed with N_2 saturated aqueous – ethanolic 0 % - 50 %) TV solutions as shown in Fig. 16 on 9 μs and 0.34 ms time scales. There the fast formation (i.e. at 9 μs) of the absorption at 350 nm showing decreased sorption on a longer time scale of 0.77 ms. The fast formation of the 420 nm absorption ak show no decrease of absorption at longer times (0.34 ms). However the absorption served in the 450 nm – 550 nm wavelength range which also forms quickly after the ctron pulse, remains on longer time scale (Fig. 16).



g. 16: Optical absorption spectra in N_2 saturated aqueous – ethanolic solutions H = 6.7) of 0.1 mmol dm^{-3} of TV taken 9 µs and 0.34 ms after the electron pulse

rmation of the tetrazolinyl radical

In general dilute N_2-saturated tert-butanol containing neutral (pH = 5.7; pH = 6.7) l alkaline (pH = 10.8) solutions of tetrazolium violet salt, an intermediate product orbing in the 300 – 500 nm region (maximum at 350 nm and another absorption peak 20 nm) was observed immediately after the electron pulse (Figs. 12, 13, 17).



g. 17: Optical absorption spectra in N_2 saturated aqueous solutions of 0.1 mmol 1^{-3} of TV containing tert-butanol taken 14 µs, 0.6 ms and 1.8 ms after the 2.6 µs ctron pulse (pH=6.7)

According to these investigations the tetrazolium radical decays in a second-order cess resulting in the final radiolysis product, the formazan as discussed later. The ay of this radical is shown on Fig. 6.7. together with the fitting curve to calculate the ond order rate constant.

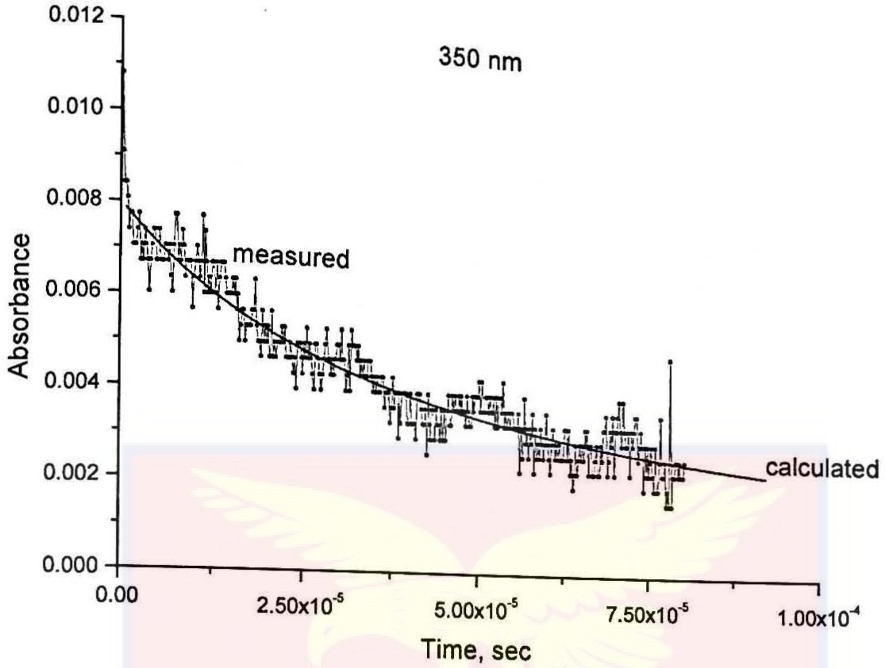
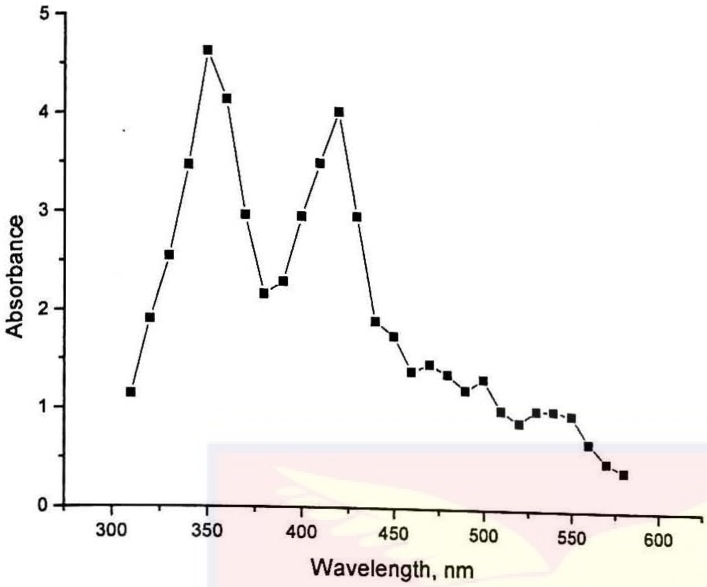


Fig. 18: Oscilloscope trace of the tetrazolium radical decay at 350 nm

In N_2 saturated tert-butanol containing neutral solutions (pH = 5.7 and 6.7) a oad absorption band appears gradually in the 450 - 580 nm region on the hundreds of and ms time scale (Figs. 12. and 17). The fast appearance of this absorption band was served in tert-butanol containing alkaline solutions (Fig. 19).



ig. 19: Optical absorption spectrum in alkaline N_2 saturated aqueous solution of .1 mmol dm^{-3} of TV containing tert-butanol taken 7 μs after the 2.6 μs electron ulse

The formation of this species, i.e. the final formazan product, became more ignificant with higher yield in the same solution (pH = 10.8) as seen on Fig. 20, where he spectra taken 10 μs and 0.77 ms after the electron pulse are compared.

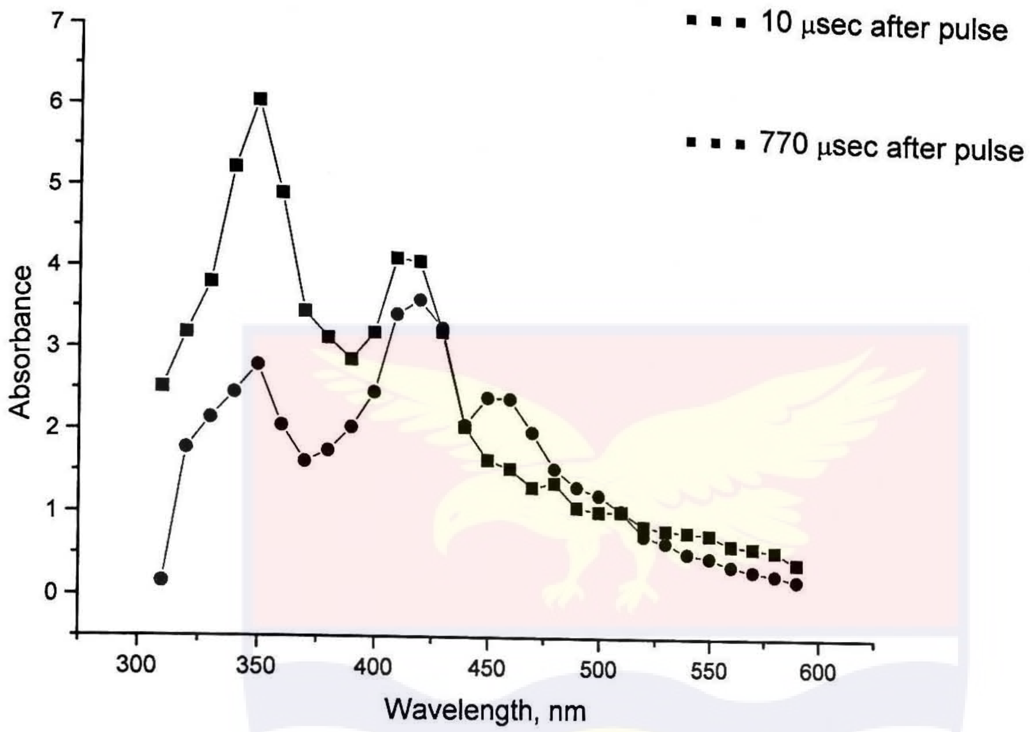


Fig. 20: Optical absorption spectra in N_2 saturated aqueous solutions of 0.1 mmol dm^{-3} of TV containing tert-butanol, taken 10 μs and 0.77 ms after the 2.6 μs electron pulse (pH = 10.8)

The oscilloscope trace of the formation of the formazan final product is shown on Fig. 21 together with the result of the fitting procedure resulting in the second order rate constant for its formation ($k = 4 \times 10^9$ dm^3 $mol^{-1}sec^{-1}$).

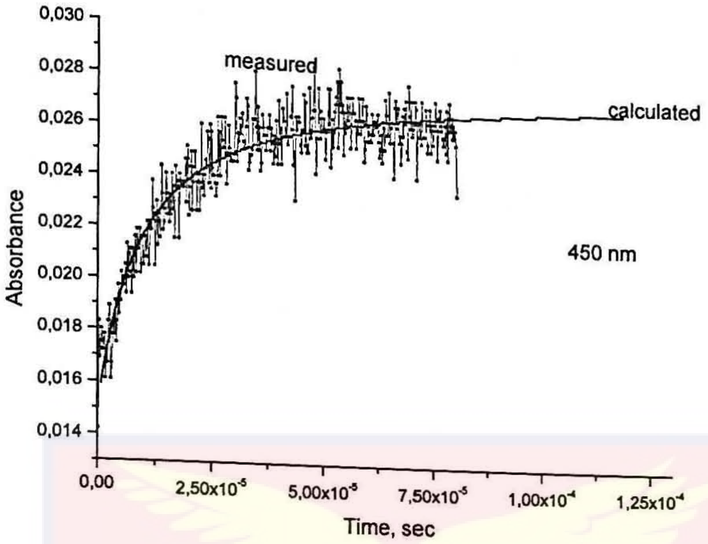


Fig. 21: Oscilloscope trace on the formation of the formazan final product

Radiolysis of TV^+ under oxidative conditions

The optical absorption spectra taken in N_2O saturated acidic (pH = 3.1), neutral (pH = 5.7) and basic (pH = 10.7) aqueous solutions were similar, showing an absorption maximum at 330 nm with a shoulder at 370 nm and a broader absorption band in the 410 – 550 nm region (Fig. 22).

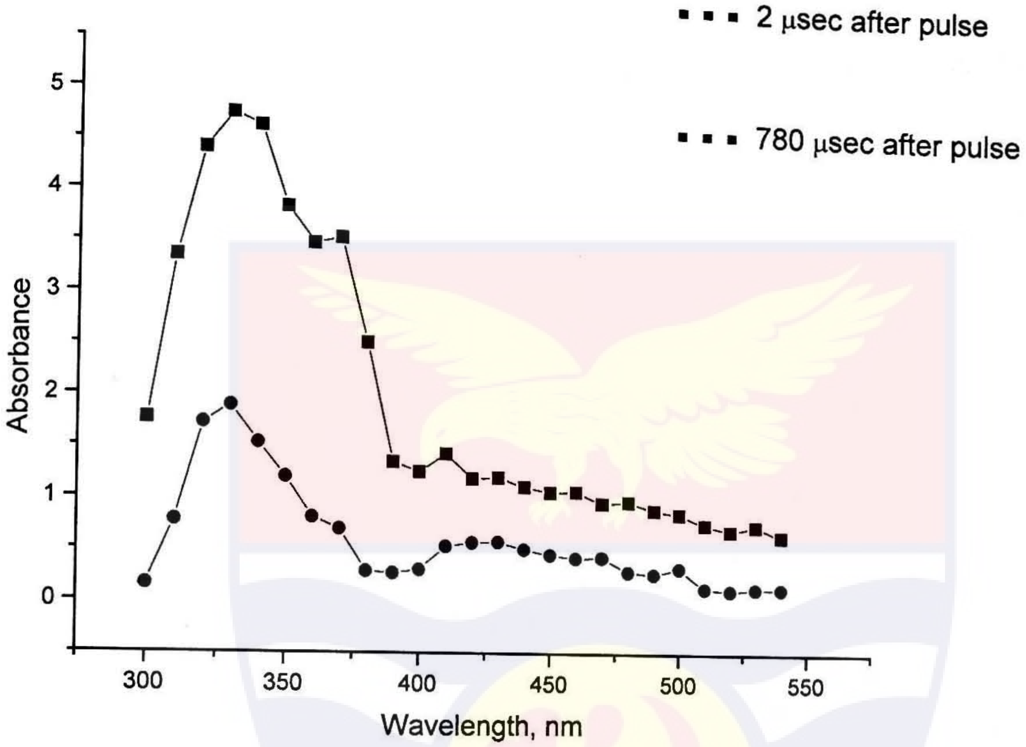


Fig. 22: Optical absorption spectra in N_2O saturated aqueous solutions of 0.1 mmol dm^{-3} of TV taken 2 μs and 0.78 ms after the 2.6 μs electron pulse (pH = 10.7)

The other broader absorption band observed in the 410 - 550 nm region also forms on the μs time-scale. This absorption remains even on the ms time-scale, thus it may be assumed that it belongs to another probably less reactive OH-adduct. As seen on Fig. 23 the spectra are similar at pH = 5.7 as at pH = 10.7, but on the longer time scale the absorption observed in the 410 – 550 nm region is somewhat stronger in the alkaline solutions.

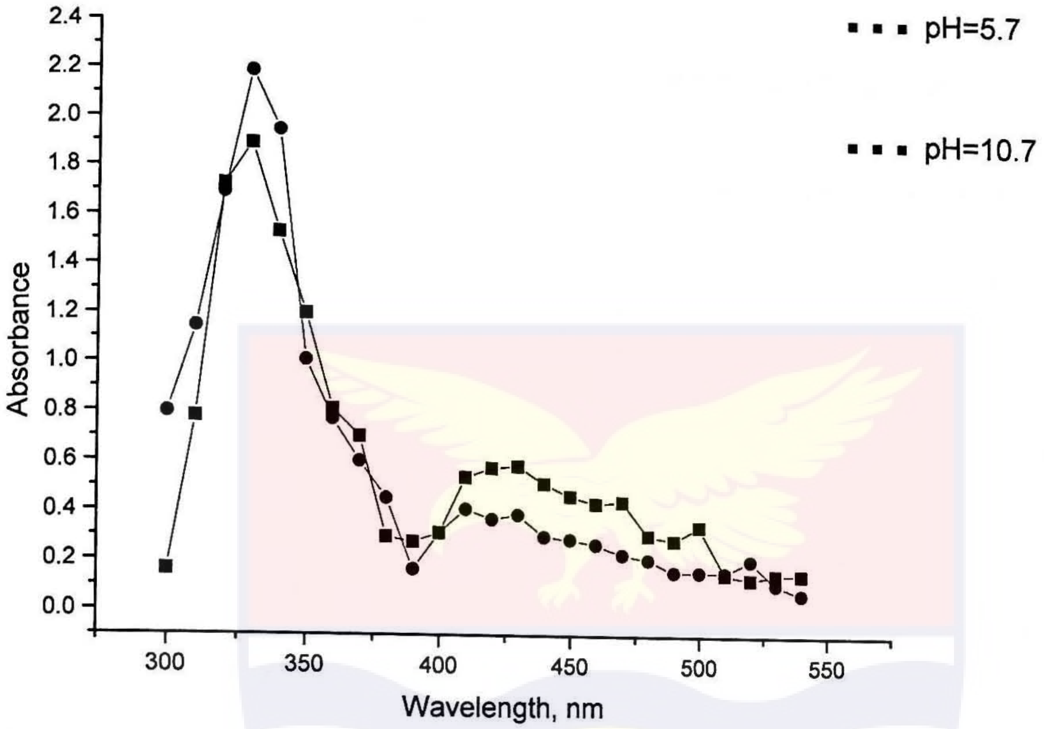


Fig. 23: Optical absorption spectra in N_2O saturated aqueous solutions of 0.1 mmol dm^{-3} of TV taken 0.78 ms after the 2.6 μs electron pulse in slightly acidic (pH = 5.7) and in alkaline (pH = 10.7) solutions

Radiolysis of TV in air saturated solutions

In air saturated slightly acidic solutions (pH = 5.7) an absorption in the UV region shows a maximum at 340 nm and a shoulder at 320 nm forms within the electron pulse (Fig. 24). The absorption observed at 340 nm decreases fast, while the one at 320 nm also decreases, but it is still present 0.78 ms after the electron pulse. Another absorption band with a maximum at 420 nm forms also within the pulse and decreases together with the 340 nm absorption band.

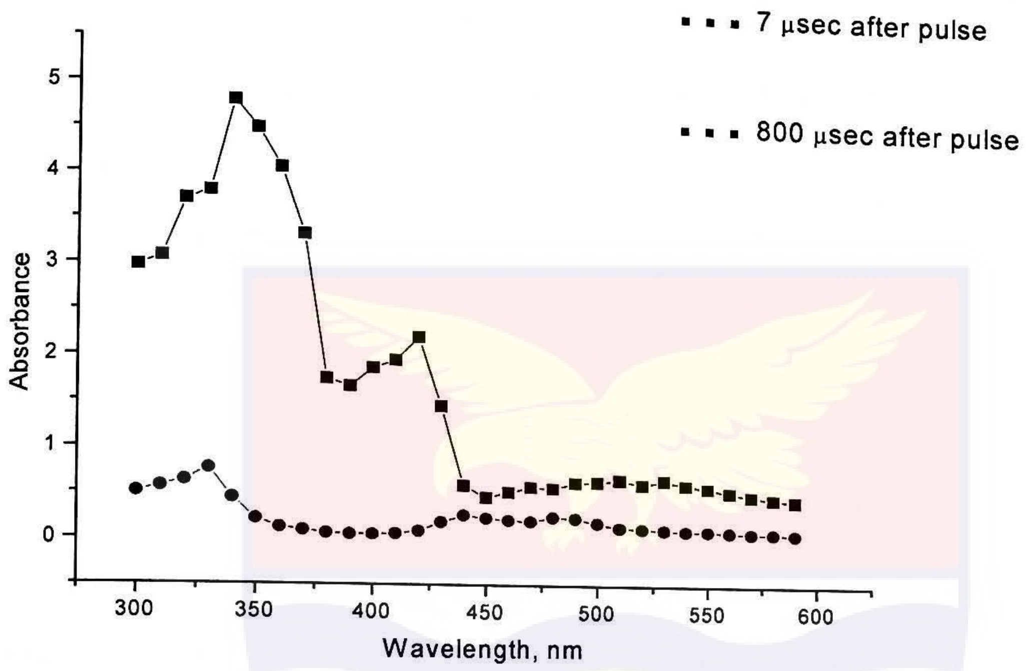


Fig. 24: Optical absorption spectra in air saturated aqueous solutions of 0.1 mmol dm^{-3} of TV taken 7 µs and 0.78 ms after the 2.6 µs electron pulse in slightly acidic (pH = 5.7) solutions

Another broad absorption band in the 440 – 600 nm region forms fast being already present a few µs after the pulse, and remains still at 0.78 ms with two maxima at 440 nm and 480 nm. These latter absorption maxima are supposed to be responsible for the formazan formation under such conditions.

The absorption spectrum taken in air saturated solutions show similarities to the one taken in N_2O saturated solutions on ms time scale supporting the assumptions of the formation of OH-adducts (Fig. 25).

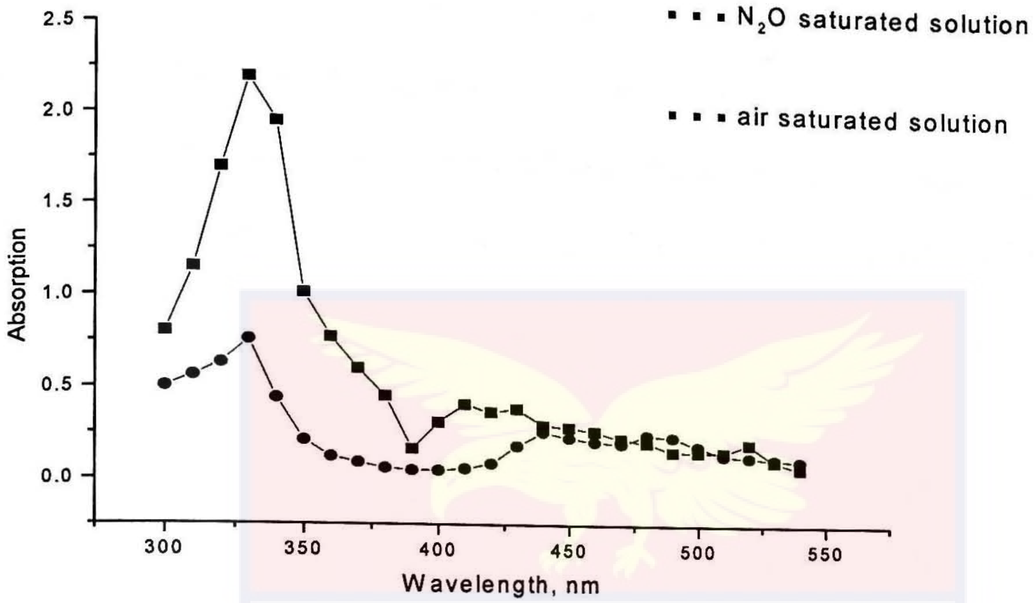


Fig. 25: Optical absorption spectra in air and N_2O saturated aqueous solutions of 0.1 mmol dm^{-3} of TV taken 0.78 ms after the 2.6 µs electron pulse in neutral (pH = 5.7) solutions

Gamma radiolysis investigations

In order to study the potential dosimetry characteristics of tetrazolium violet for gamma doses, aqueous, aqueous – alcoholic, alkaline and acidic solutions were investigated by gamma radiolysis. The reduction of the salt in aqueous solution was followed to determine if the reaction of TV in solutions agree with the observations made by Kriminskaya et al in 1984.

Radiolytic reactions of TV in aqueous solutions

The neutral air saturated TV solution changes colour from pale yellow to pink with intensity depending on the dose given, becoming deeper with increasing dose. The optical absorbance response begins to show up at 500 Gy. The optical absorption spectrum of the unirradiated and irradiated 1mM solutions to varying doses of TV show pronounced absorption band at ~ 516 nm with a shoulder in the range between 530 – 560 nm (Fig. 26).

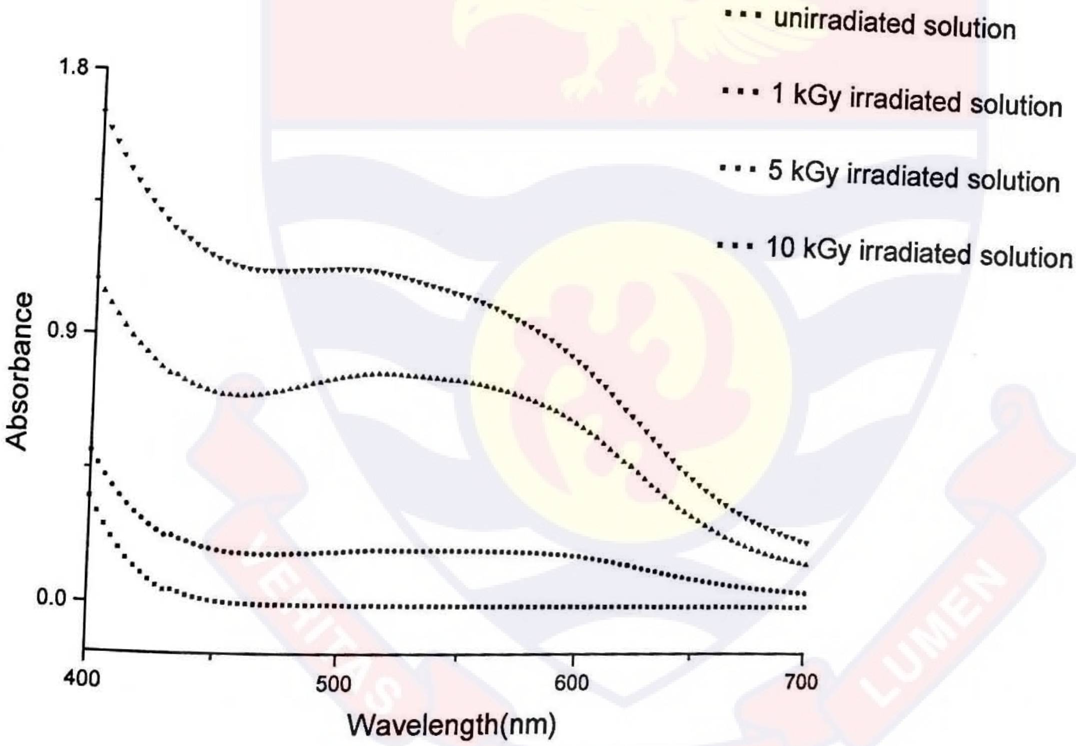


Fig. 26: Absorption spectra of 1mM TV solution (pH=5.6) irradiated up to 10 kGy

The optical absorption spectra of the air saturated aqueous solution of 1 mM TV with a pH of 5.6, unirradiated and irradiated to doses from 0.5 kGy to 15 kGy are shown in Fig. 27. On the basis of the pulse radiolysis measurements as well as the published absorption spectra in the literature (Kovacs et al, 1999; Pikaev and Kriminskaya, 1995; Kovacs et al (1996), the radiation induced absorption in the visible spectrum showed a maximum at around 516 nm and a shoulder at about 550 nm.

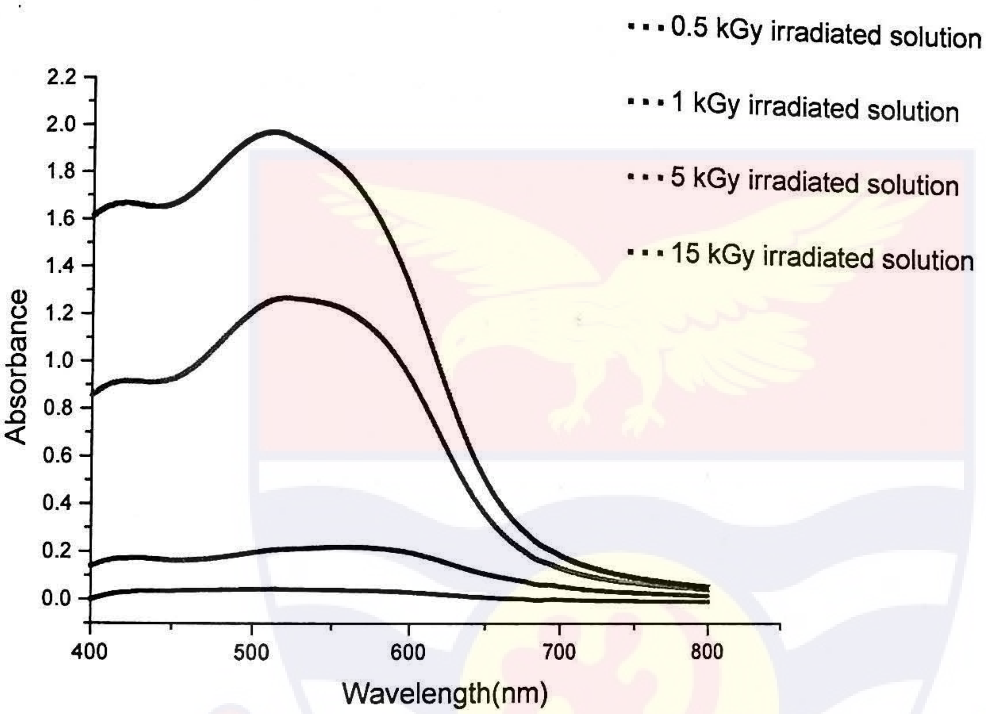


Fig. 27: Optical absorption spectra of aqueous 1mM TV solution.

Dependence of absorbance on concentrations of TV solutions

The colour change is deeper for the high concentration solutions for the same given dose. As a consequence the peak absorbance of the different concentrations of the TV solution differ for the same radiation dose i.e. higher absorbance values are recorded for higher concentration solutions when irradiated to the same dose. Fig. 28, shows the absorbance change with concentration for the same given dose of 5kGy. It reveals the sensitivity of the aqueous solutions of TV with concentration and on the other hand the significant observation made from the spectra is the shift of the absorbance peak towards longer wavelengths with increased concentration.

Studying the effect of TV concentration on the formazan formation in aqueous solutions (pH = 6.24) at concentrations of 0.5 mM, the absorbance at 530 nm was found to increase up to a dose of 750 Gy followed by a decrease with increasing dose when all the TV may have been used up. When using 1 mM TV solution the decrease of the formazan radiolysis product goes beyond 50 kGy, while for 2 mM TV solutions the absorbance measurements go out of scale of the U-V spectrophotometer at doses beyond 15 kGy. The high absorption of the radiolysis product (i.e. formazans) for high concentrations of TV required dilution of the irradiated solutions in order to get measurable absorption values with the spectrophotometer.

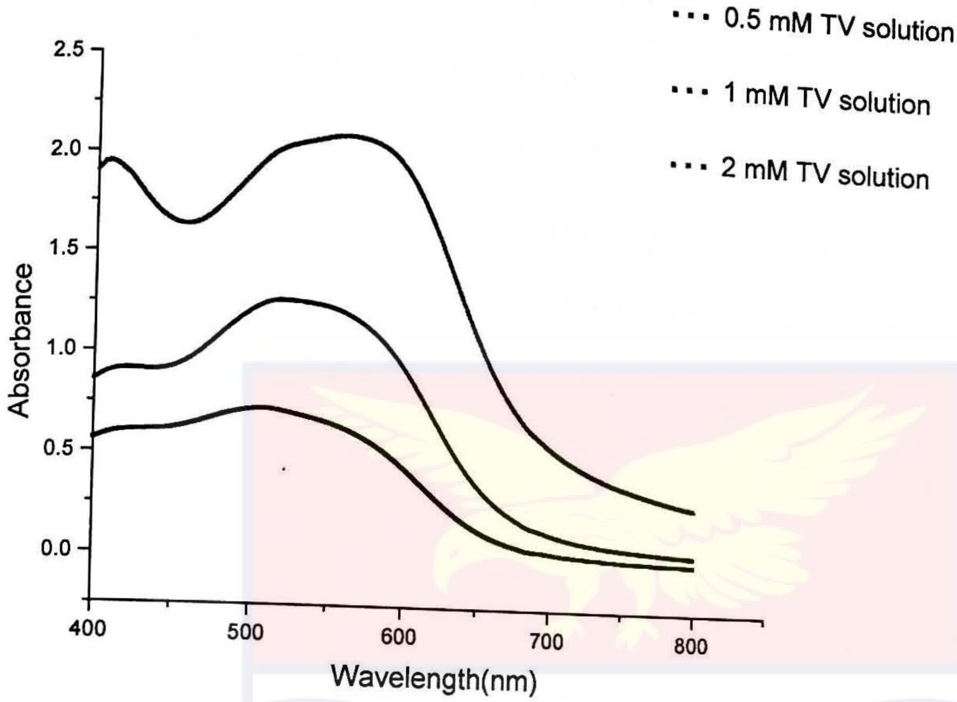


Fig. 28: Different concentrations of TV solution irradiated to 5kGy.

Effect of pH on TV solution

To study the effect of pH on the formation of formazan, aqueous solutions containing 1 mM TV were prepared with different pH values (i.e. with pH range of 3.34 – 10.35). The irradiation of the solutions reveal colour changes which are different from the neutral solutions. For the low pH (i.e. 3.34) the pale yellow solution turns brownish pink and precipitates at 1 kGy. It was also observed that the unirradiated solution even precipitates under ordinary laboratory conditions after 24 hours under laboratory conditions. The high pH (i.e. 10.35) become greenish black on irradiation and also precipitates at 1 kGy. The solution turns colourless at 10 kGy. The shape of the spectrum for the pH = 3.34 solution (Fig. 29) is similar to the one observed for pH = 5.6, although in the strong acidic environment only a shoulder appears at 600 nm with a much smaller absorption. The spectrum of the solution with pH = 10.4 is much more pronounced and has higher absorbance values as compared with the acidic and neutral preparations. In all cases the prominent peaks are in the neighbourhood of 600 nm.

From these investigations, precipitation appears in alkaline solutions even at low doses of 1 kGy, while in slightly acidic solutions and at similar low doses no precipitation was observed until after a few hours after irradiation.

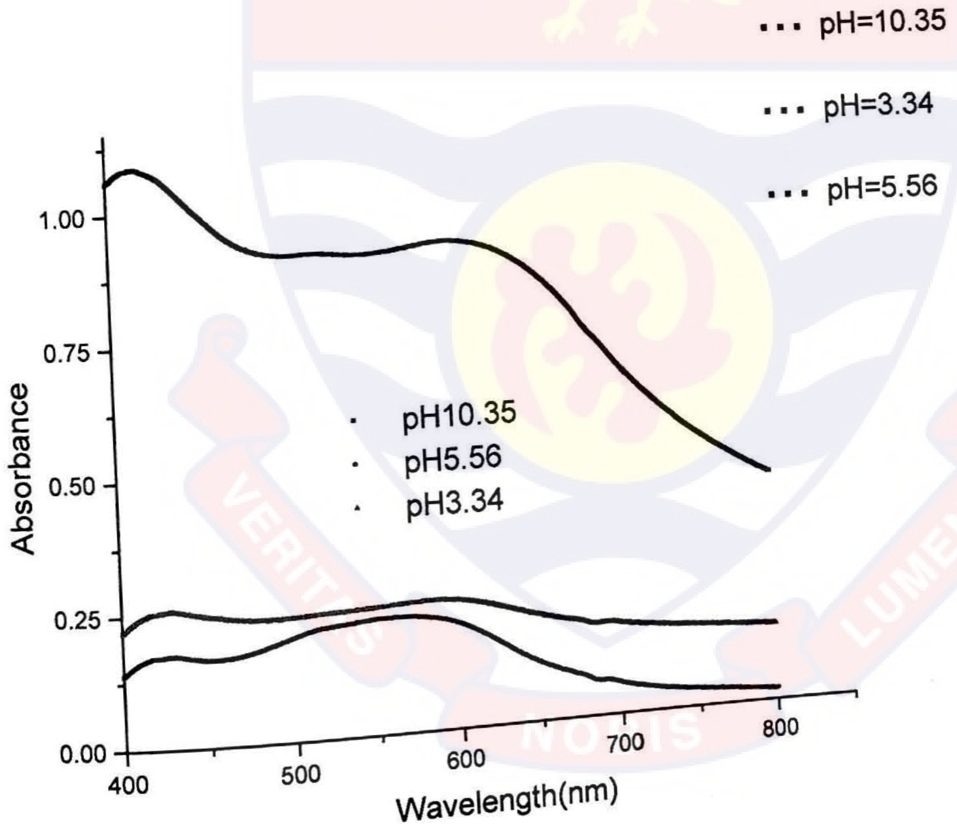


Fig. 29: Effect of pH on TV solutions irradiated to 10kGy at 15kGy/hr

Radiolytic reaction of aqueous – alcoholic solution

The formation of the radiolytic products in solutions containing ethanol showed that at low doses ~ 250 Gy, the solutions change colour as with the aqueous solution to light pink. If the solution is saturated with N_2, the pink colour obtained for the same 250 Gy is much deeper confirming the general effect of nitrogen in eliminating the inhibitory effect of oxygen (Fig. 30). However, contrary to all published works, the formazan formed from tetrazolium violet in alcoholic solutions produces greenish black precipitate at 5 kGy. The spectrum can only be obtained after dissolving the precipitate in water or chloroform.

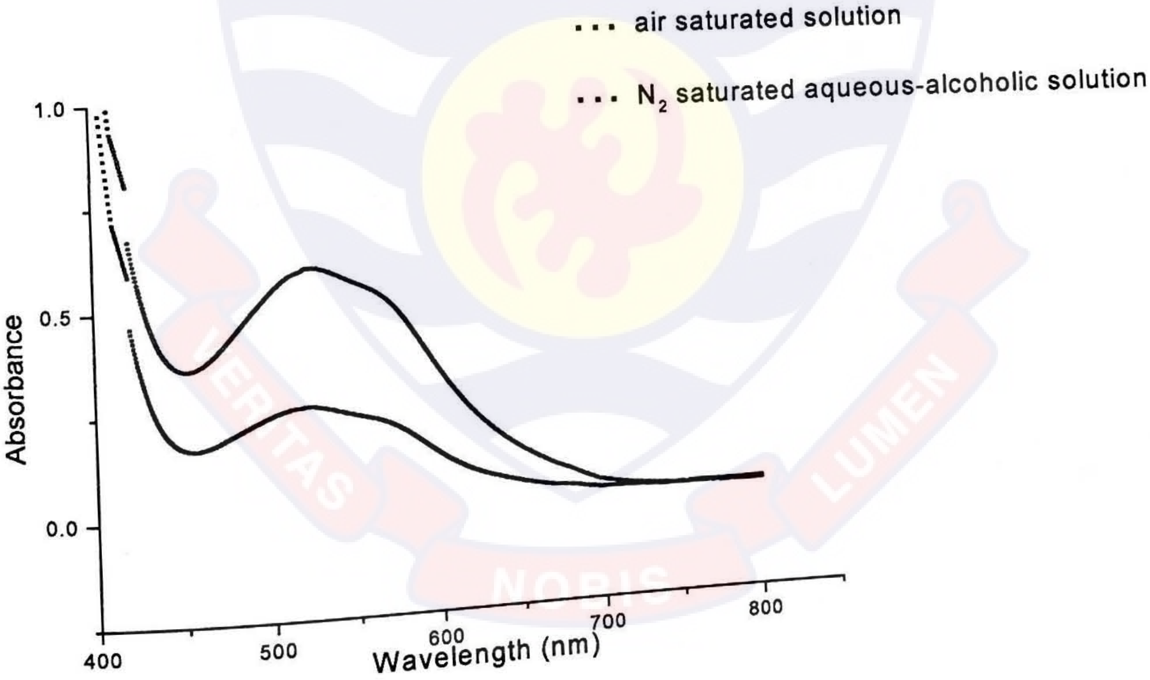


Fig. 30: Response of air saturated and N\-(2) saturated aqueous-alcohol solutions of tetrazolium violet

Radiolytic reactions of TV in aqueous – t-buthanol solutions

According to the investigations of Kriminskaya et al (1983), the radiolytic reduction of tetrazolium salts (e.g. the 2,3,5 – triphenyl – tetrazolium chloride) is more pronounced in the presence of alcohols (like ethanol or isopropanol), since not only the hydrated electrons take part in the reduction process, but also the hydroxyalkyl radicals, formed from the alcohols as well. Additionally, the solubility of the formazans as radiolytic products was better in alcohols, than in aqueous solutions. Therefore the radiolysis of the TV was investigated in aqueous solutions containing 50% by volume of t-buthanol in 1mM aqueous solution. The solution was air saturated at a pH of 6.24. The solution changes colour from the usual pale yellow colour to light pink at 500 Gy, but with some precipitate. The colour change and precipitate become pronounced with increased dose but begin to disappear at 15 kGy.

The optical absorption spectra of the solutions irradiated to 5 kGy showed absorption maximum at ~ 515 nm without the shoulder at 560 nm as shown in Fig. 31. If compared with the aqueous solution, it is observed that there is a conspicuous shoulder at about 570 nm.

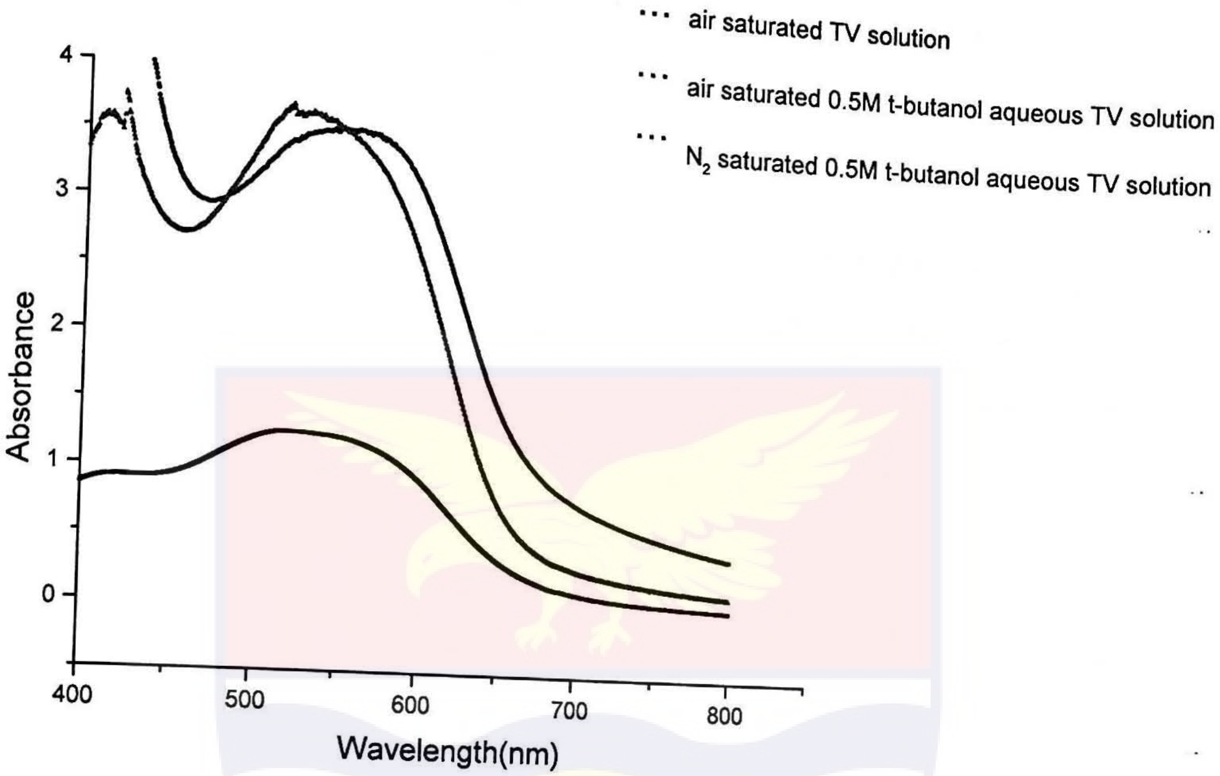


Fig. 31: Effect of t-butanol on response of 1mM TV solutions irradiated to 5kGy.

Effect of Nitrogen saturation on irradiation of TV solution

Since the process leading to the formation of the coloured formazan is radiolytic reduction, 1 mM TV solutions saturated with N_2 and N_2 saturated solution containing t-butanol all intended to reduce or eliminate the inhibiting effect of oxygen in the process were investigated. The optical absorption spectra of the aqueous N_2 saturated TV solutions with and without t-butanol are shown in Fig. 30 - Fig. 32. They are found to be similar to the air saturated solutions. Also similar to the effect of pH variations, the N_2 saturation significantly increases the response with respect to dose. The absorbance at 516 nm was noted to be 0.024 for the air saturated and 0.106 for the N_2 saturated solutions when the solutions were irradiated to 250 Gy. Similarly the absorbance at 516 nm was 1.283 and 1.75 for the air saturated and N_2 saturated respectively at a dose of 5 kGy.

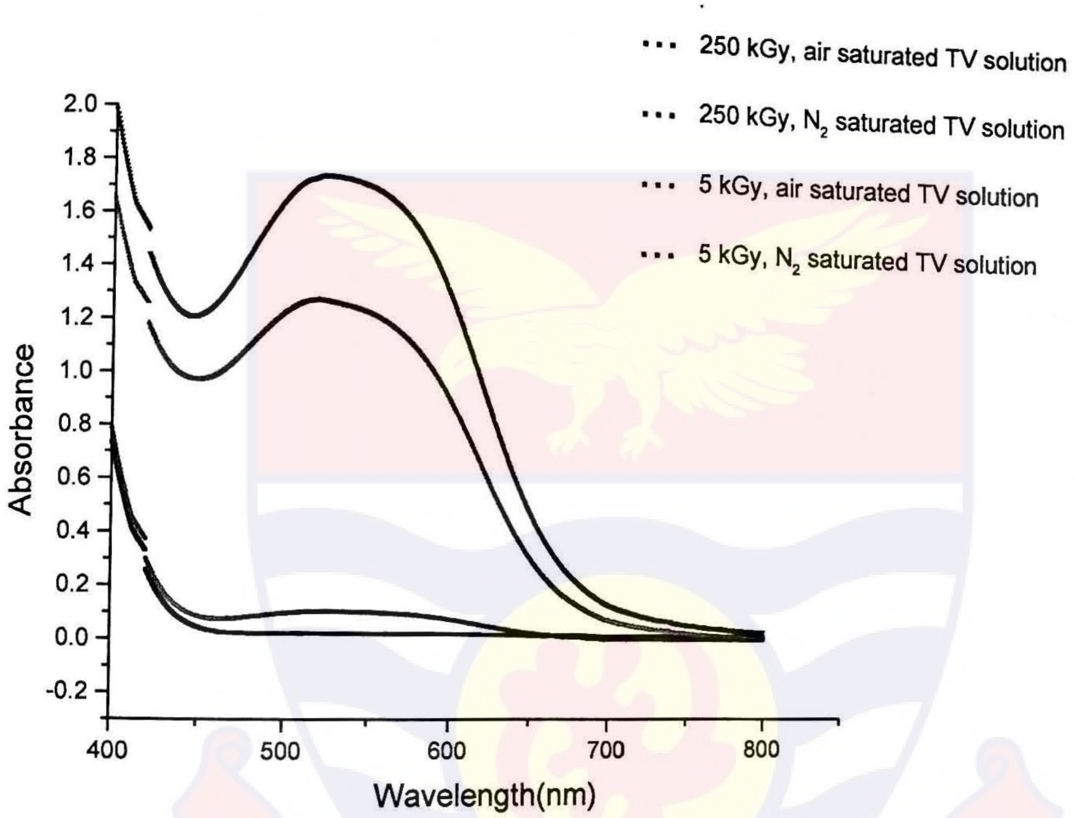


Fig. 32: Comparative Response of Air saturated and N\-(2) saturated TV solutions to Radiation Dose

Stability of formazan formed after the irradiation

The time dependence of the absorbance values or stability of formazan formed was investigated with 1mM TV solution and shown in Fig. 33 below. It was observed that the absorbance at 506 nm immediately after irradiation was 0.204, and remained virtually the same after 1 hour but rose to 0.207 (i.e. +1.5%) 2 hours after the irradiation.

The absorbance at 500 nm reached its maximum of 0.245 (i.e. + 20%) after 24 hours but decreased thereafter to 0.225 (i.e. +10%) of the initial readings after 1 week. These results indicate that the reduction of the TV solution is not completed immediately after the irradiation until after 24 hours but undergoes fading with respect to the absorbance reaching 10% of the initial reading one week after the irradiation.

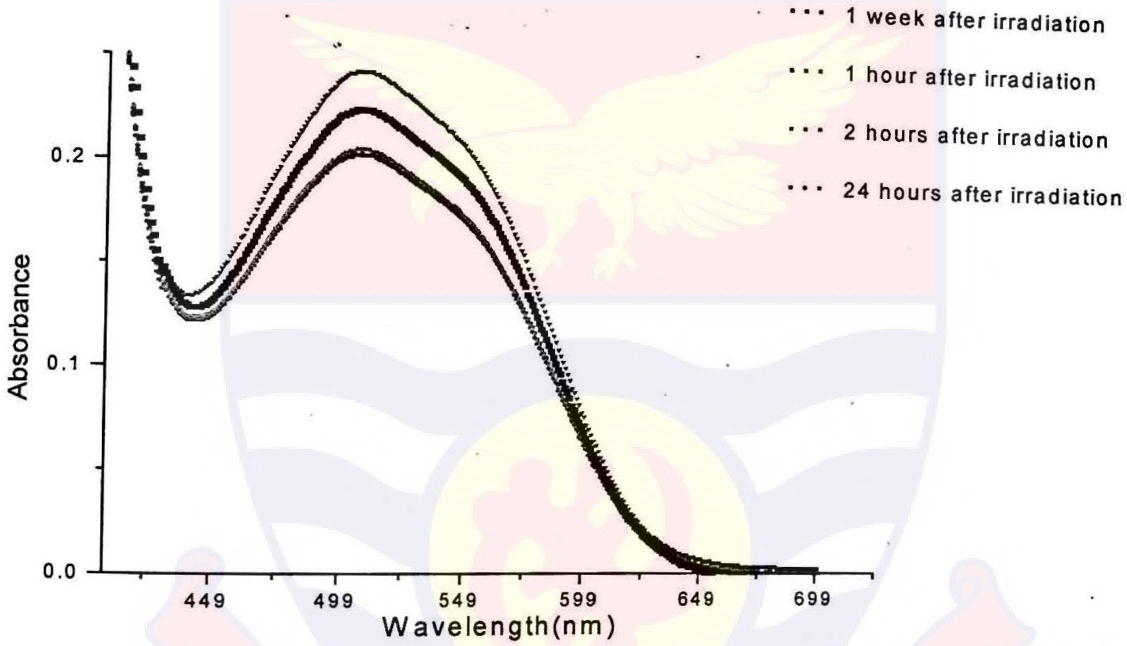


Fig. 33: **Dependence of absorbance on time after irradiation**

Dose rate effect on the response of TV solution irradiated to 5kGy

Since the reduction process continues for some time after the irradiation, it is apparent that the process would also be dose rate dependant. The dose rate effect of the response of the irradiated TV solution to the same dose of 5 and 30 kGy were investigated with 1mM TV solution and the results shown in Figures 34 and 35. At the dose of 5 kGy the absorbance of the 1 mM TV solution was relatively higher for the 1kGy/h than for the 15kGy/h. Additionally one observes a pronounced shoulder with the

1 kGy/h as compared with the 15 kGy/h spectrum. As seen from Fig. 35 the

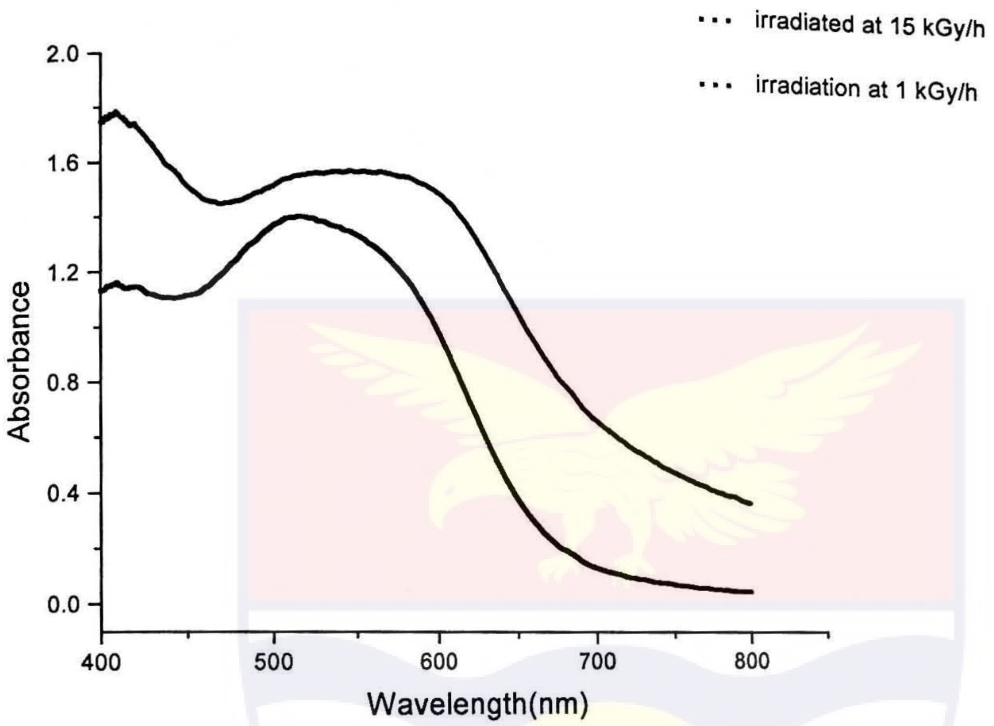


Fig. 35: Dose rate effect on the response of TV solution irradiated to 5kGy

absorbance spectra at 30 kGy almost overlap, for the different dose rates, at the peak wavelength of 506 nm.

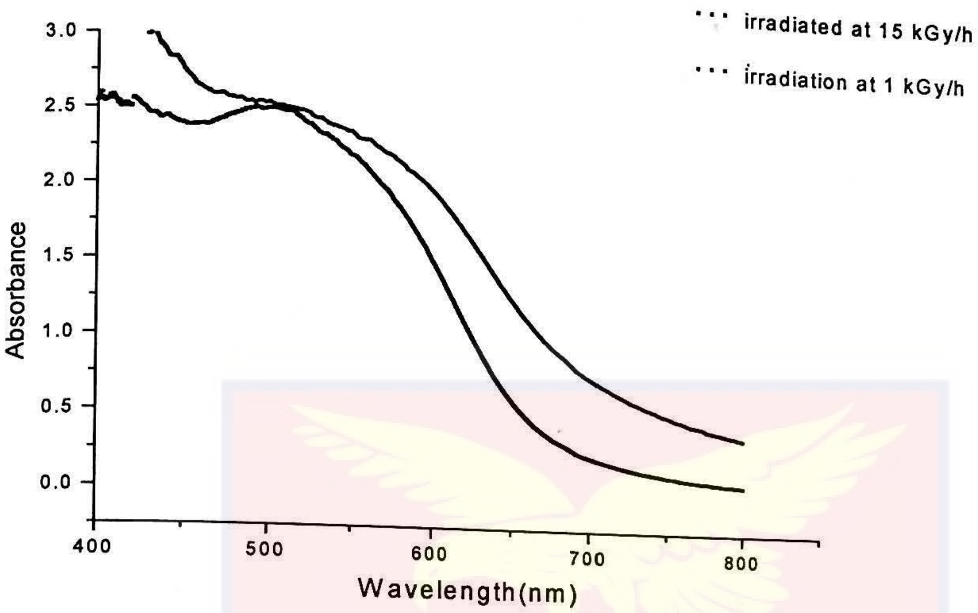


Fig. 36: Dose rate effect on the response of TV solution irradiated to 30kGy

Effect of temperature on the measurement of absorbance of TV solution

The effect of temperature on the readout of absorbance values was investigated from 10 °C to 60 °C for the solution irradiated to a dose of 5 kGy. Fig. 36 and Table 1 show the behaviour of the absorbance measurements varying with the temperature of the TV solution. The absorbance decreases from 10 °C to 30 °C but only slightly increases between 30 °C and 60 °C. The maximum absorbance occurs at 10 °C with the value of 1.683 i.e. 16.1% over the value at 25 °C whereas at 60 °C the absorbance is 1.405. During these investigations, the ambient temperature was ~ 28 °C.

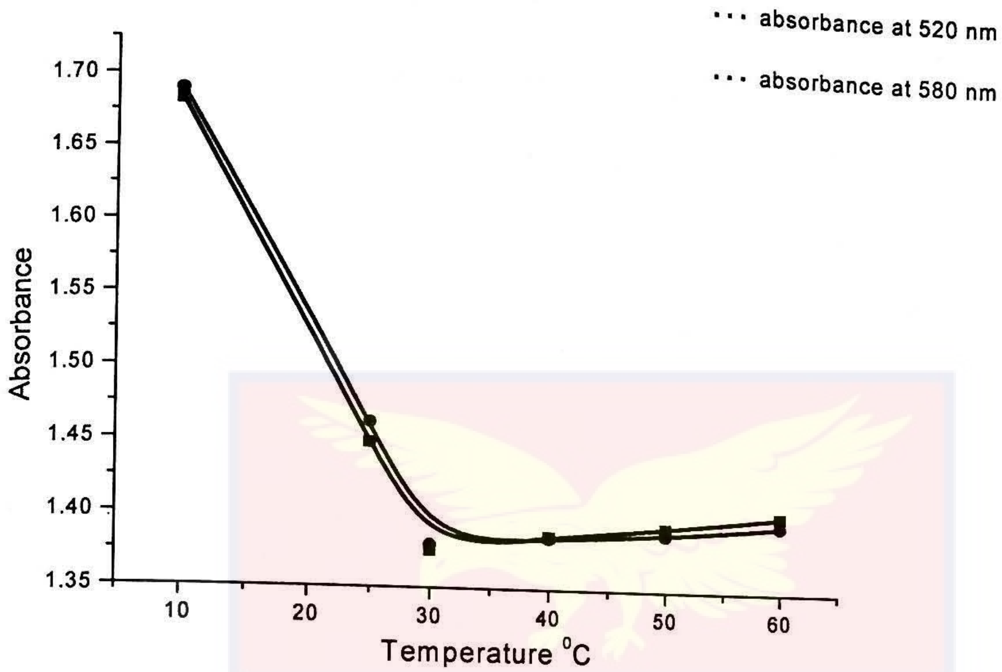


Fig. 36: **Temperature versus Absorbance for 1mMTV solution irradiated to 5kGy**

Temperature °C	Absorbance(A) at 520nm	% deviation from A at 25 °C
10	1.683	+16.1
25	1.45	-
30	1.376	-5.1
40	1.387	-4.3
50	1.395	-3.8
60	1.405	-3.1

Table 1: Absorbance changes with temperature of TV solution irradiated to 5 kGy.

Calibration of 1mM TV solution

The curves below Fig. 38 and 39 represent the calibration of the 1mM TV solution for doses up to 10 kGy and 50 kGy respectively at the absorption peak of 504 nm.

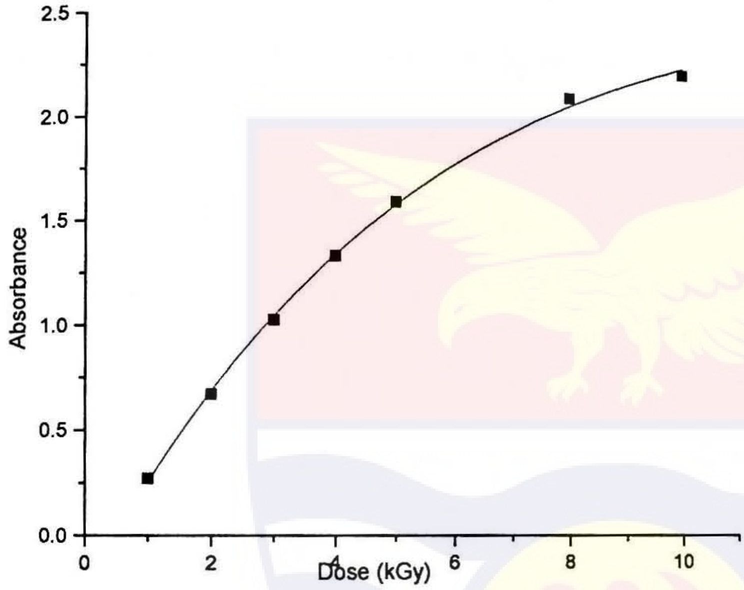


Fig. 37: Absorbance versus Dose (kGy) for TV solution for doses up to 10 kGy

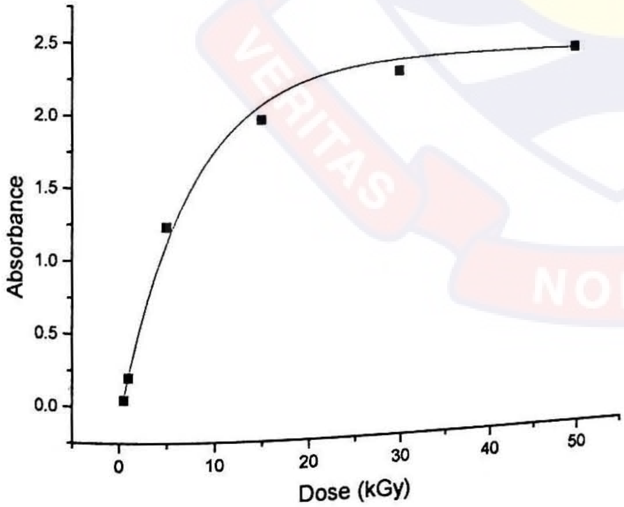


Fig. 38: Absorbance versus dose (kGy) for 1 mM TV solution

The characteristics of polyvinyl alcohol film containing TV

The films were characterized using mainly the colour change and absorbance measurements as with the solutions. The colour change in all cases was from colourless to violet depending on the dose delivered.

Characteristics of the PVA-TV film by evaluating absorbance

The absorbance spectra of the prepared films were observed over a period of 7 days as they were exposed to laboratory lighting, direct and indirect sunlight to establish the influence of these conditions on the films. Fig. 39 shows the spectra of the film first prepared without the TV radiochromic dye, exposed to laboratory lighting for 7 days. The PVA without the dye has absorbance values which appreciate slightly but no peak was observed over the 200 – 800 nm wavelength range. Contrary to this observation, the 0.5mM TV film (Fig. 40) shows a reduction of absorbance values over the period of 7 days for the same wavelength range. Similarly however, there was no peak.

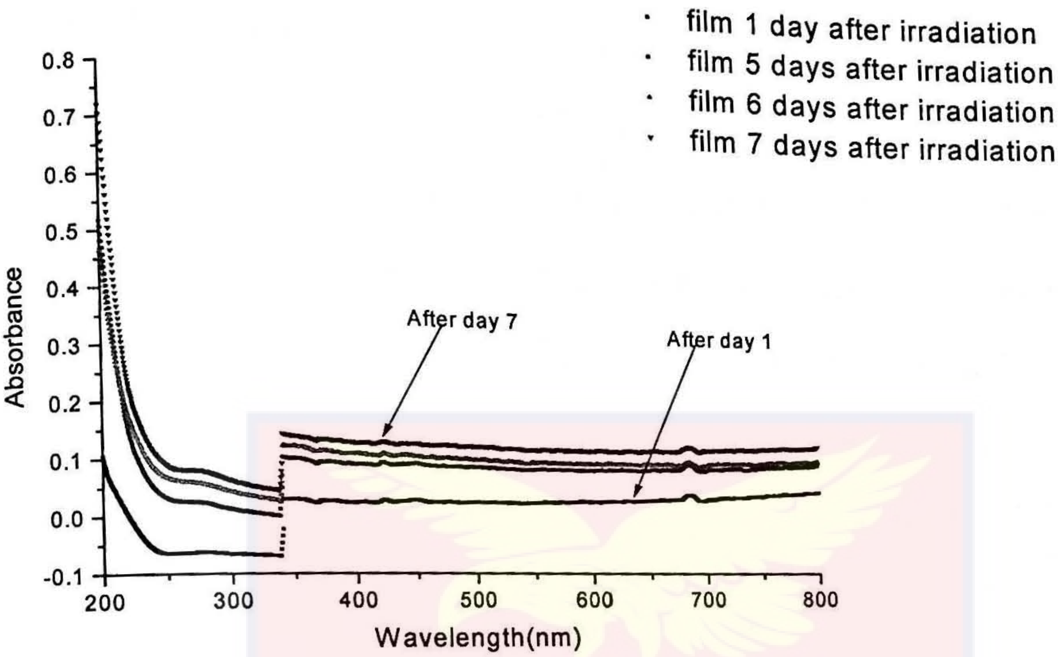


Fig. 39: Response of PVA without TV to laboratory illumination.

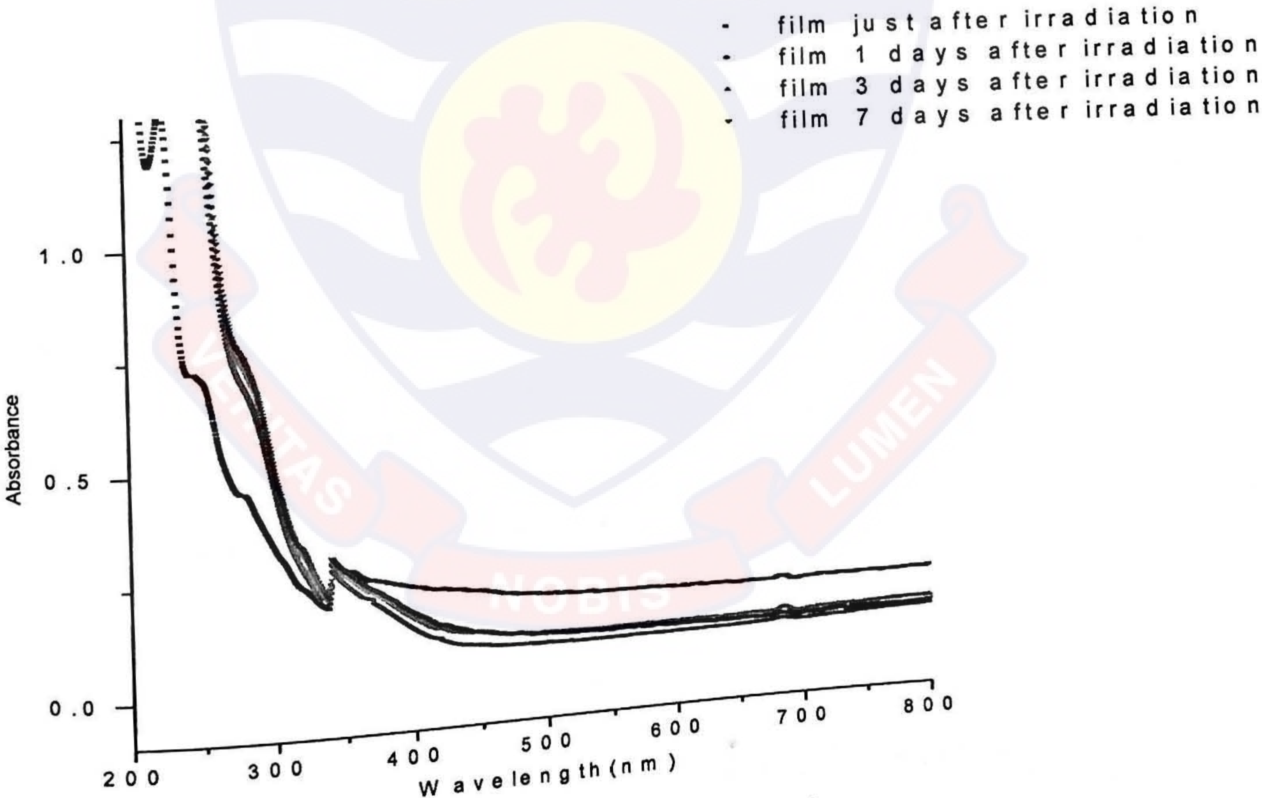


Fig. 40: Response of 0.5mM TV film to laboratory illumination

Performance of aqueous TV prepared films

The absorption spectra of gamma irradiated "aqueous" TV films prepared from TV solutions of 0.5 and 0.1 mM are shown in Fig. 41 and 42. With increasing dose, the colour of the film turns violet as observed in the case of the solutions with absorption maximum occurring at ~ 525 nm. The colour change also depends on the concentration of the TV in the film and the dose rate. The higher the concentration of the TV in the film the higher the absorbance at 525nm for the same ginner dose. For instance it was found to be 0.159 as against 0.112 for the 0.5 mM and 0.1mM TV film respectively both irradiated to a dose of 5 kGy.

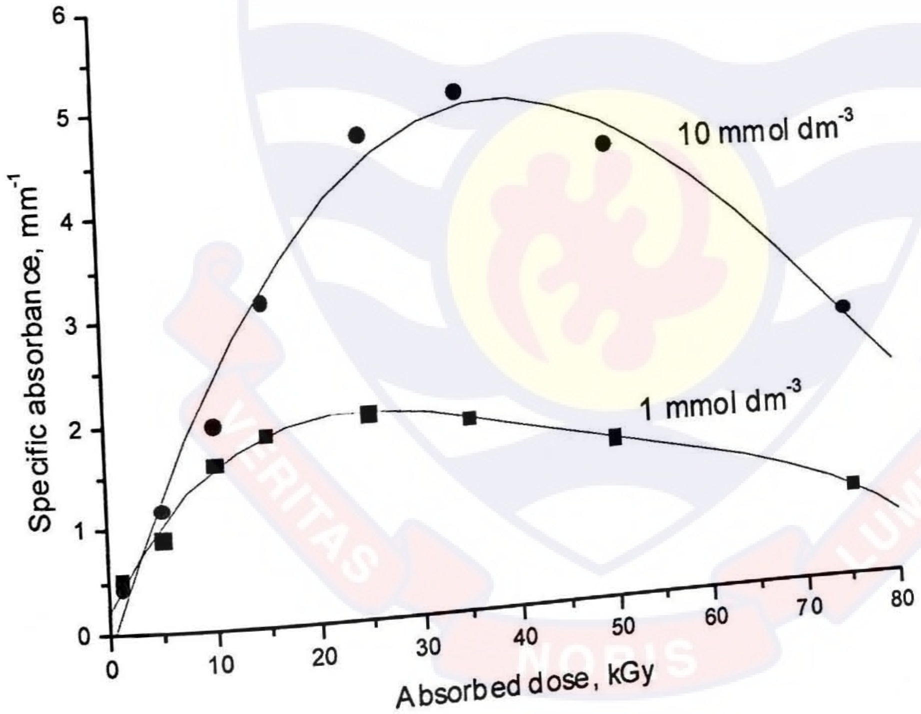


Fig. 41: Specific Absorbance of 1mmol dm^{-3} and 10 mmol dm^{-3} films to dose

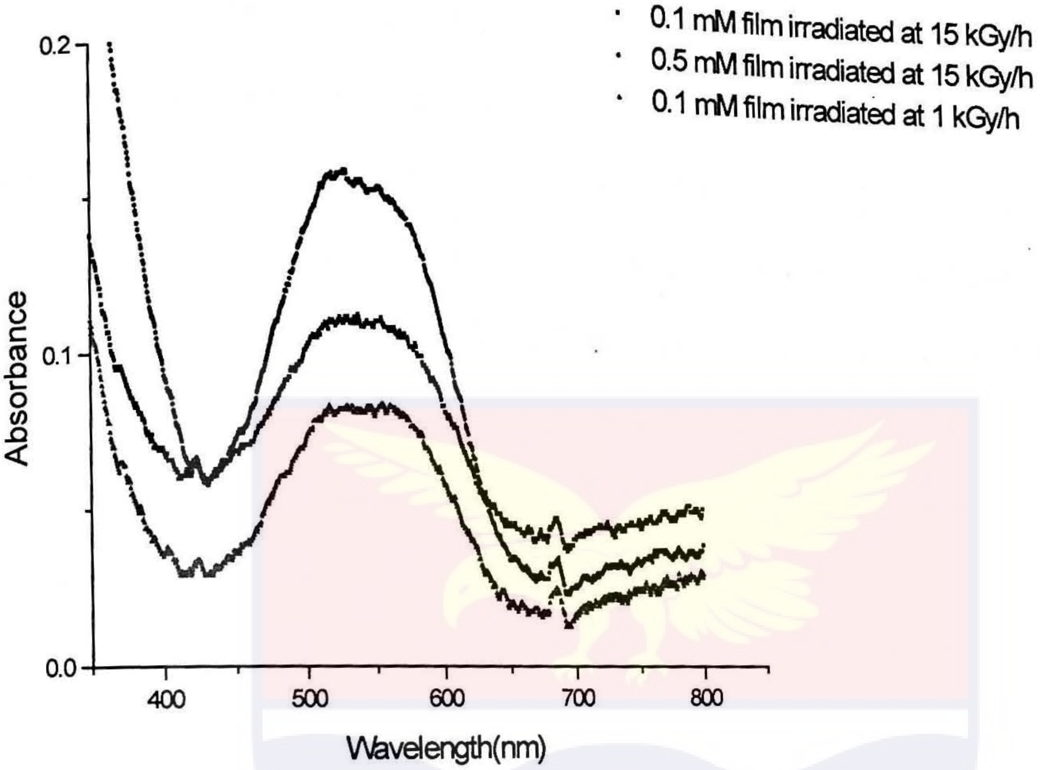


Fig. 42: Response of TV film of different concentrations irradiated to 5 kGY

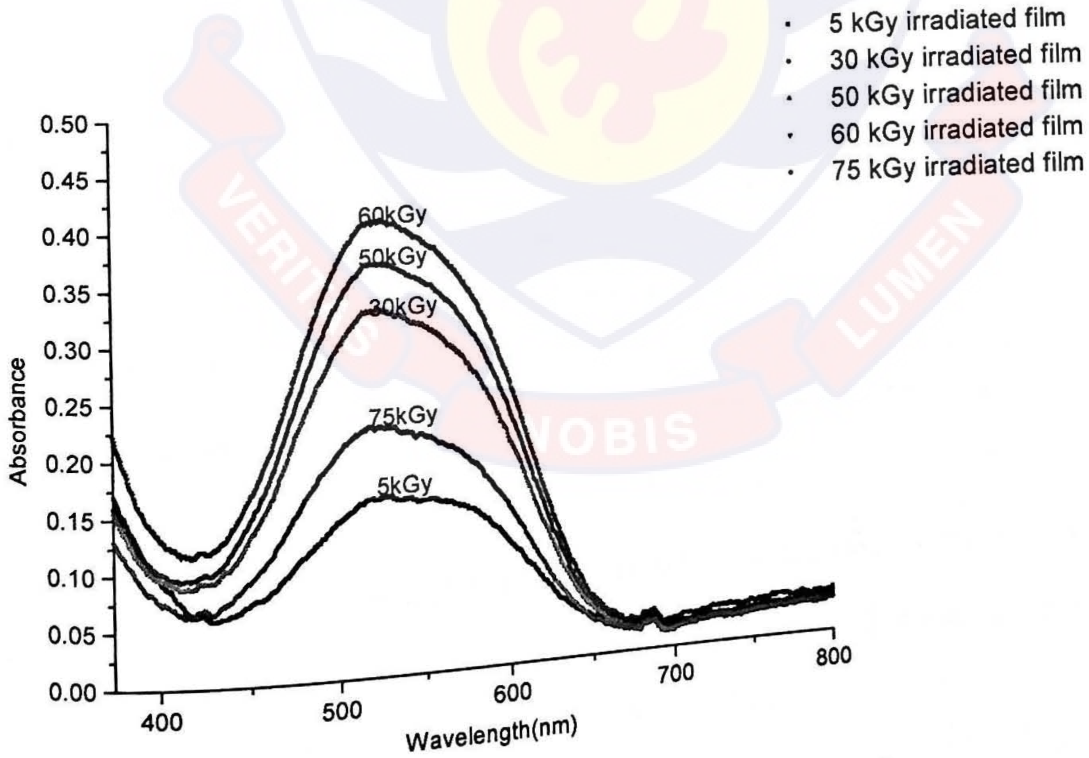


Fig. 43: Response of 0.5mMTV films to varying doses at 15kGy/hr

Comparing the films containing 0.5 – 0.2 –0.1 mM TV dye, the measurable maximum dose increases with increasing concentration, implying that a wider measurable dose range may be obtained by using higher concentrations of the solution in the preparation of the film. Higher concentrations of the TV solution also result in higher absorbance for any given absorption peak for the same absorbed dose. The spectra of the 0.5 mM TV film as shown in Fig. 43 indicates higher absorbance peaks for increasing doses up to 60 kGy. The spectrum of the 75 kGy irradiated film is observed to have a lower peak value than the 30 kGy irradiated film.

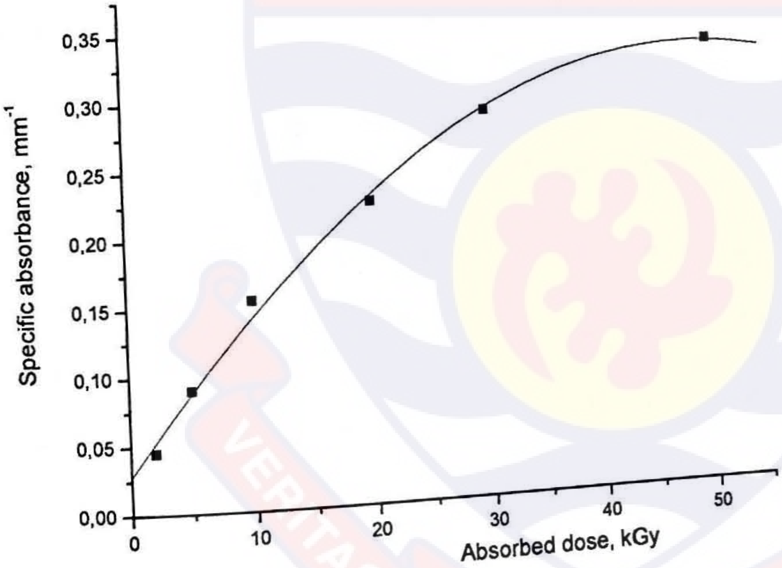


Fig. 44: shows the absorbance at 525 nm for varying doses up to 50 kGy.

The dependence of the response on the dose rate of the radiation field is shown in Fig. 45 which shows two films irradiated to the same dose of 5 kGy but at two different dose rates of 1 kGy/h and 15 kGy/h.

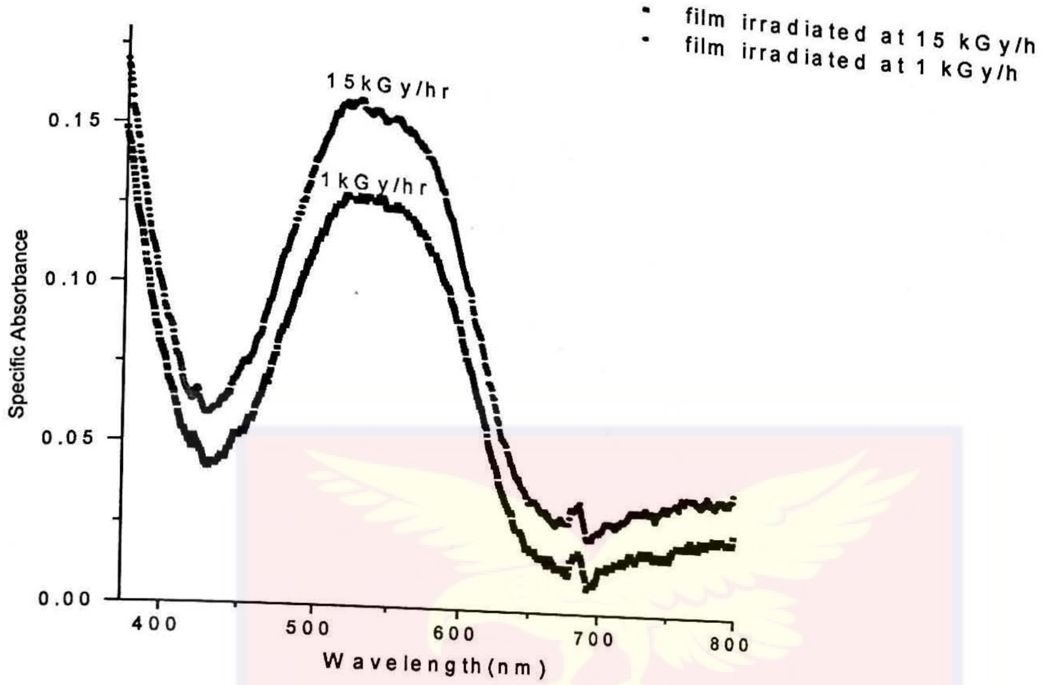


Fig. 45: Doserate response of 0.5mM TV films.

Performance of aqueous ethanol TV prepared films

When the films were prepared of aqueous – alcoholic solutions containing the TV, significant increase of the measured absorbance for a given dose was observed as shown in Fig. 46. The peak appears around 540 nm which agrees with that observed in the case of films prepared from aqueous TV solutions. However the maximum dose measurable from the spectra is 6 kGy.

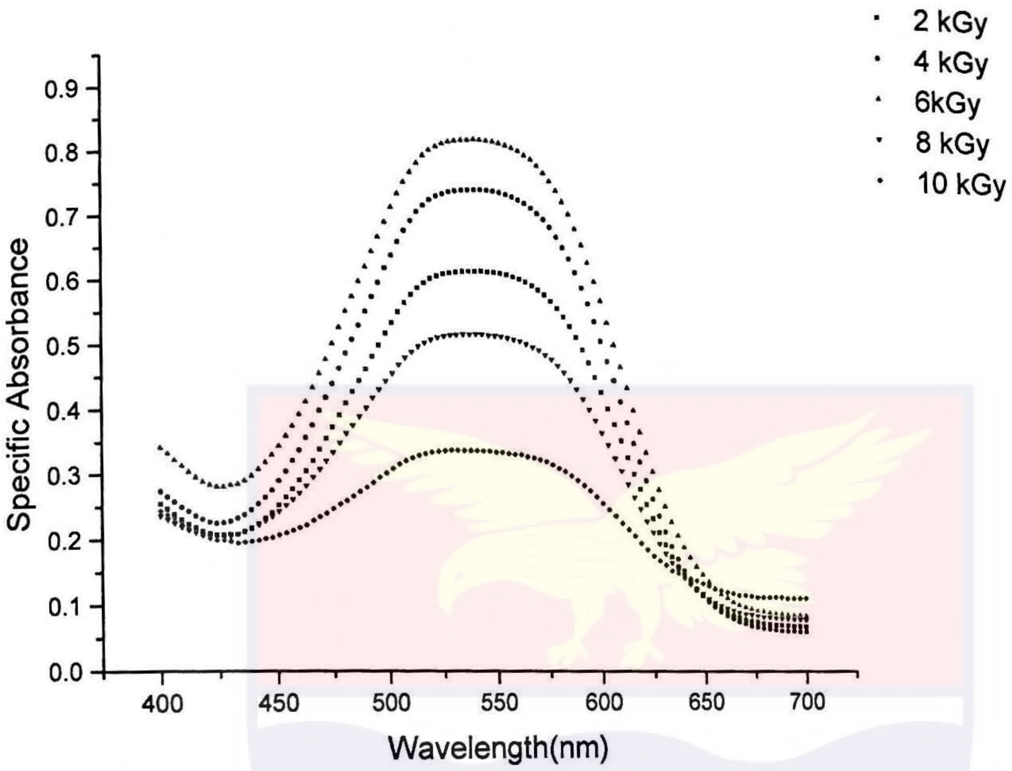


Fig. 46: Response of ethanol prepared film

Dose response of TV film prepared from low pH aqueous solution

The response of film, prepared from low pH (i.e. 3.34) TV aqueous solution to gamma irradiation is shown in Fig. 47 for doses from 2 kGy to 10 kGy. The peak is observed around 550 nm which is quite similar to the aqueous and aqueous-ethanol prepared films.

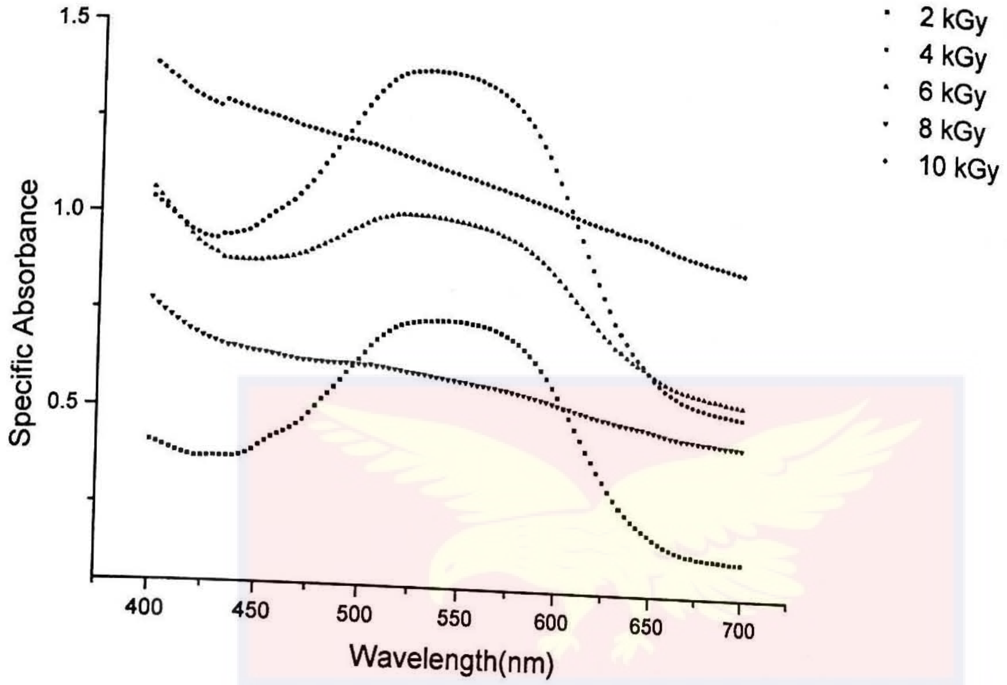


Fig. 47: Response of low pH TV prepared film to gamma radiation

Dose response of TV film prepared from high pH aqueous solution

Figure 48 shows the response of films prepared from high pH (i.e. 10.35) TV solution to gamma radiation from doses of 2 kGy to 10 kGy. Unlike all the other investigations, the spectra obtained from the high pH films show no peaks even at 2 kGy.

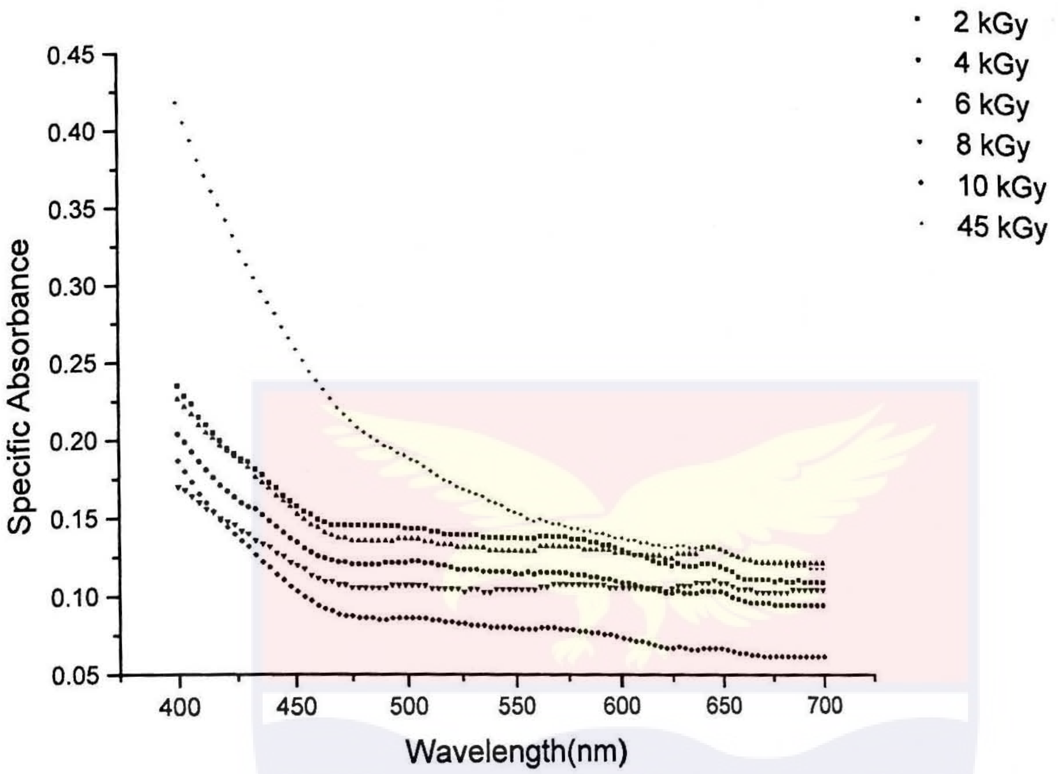


Fig. 48: Response of high pH TV prepared film to gamma radiation

Effect of Irradiation Temperature on film

The effect of the irradiation temperature on the response of these films was investigated by irradiating PVA films containing 1 and 10 mmol dm^{-3} tetrazolium violet in the 10 – 55 °C temperature range to 4 kGy and 15 kGy doses respectively. Fig. 49 shows the response of both types of films showing increasing specific absorbance (i.e. non linear) with temperature for the doses chosen.

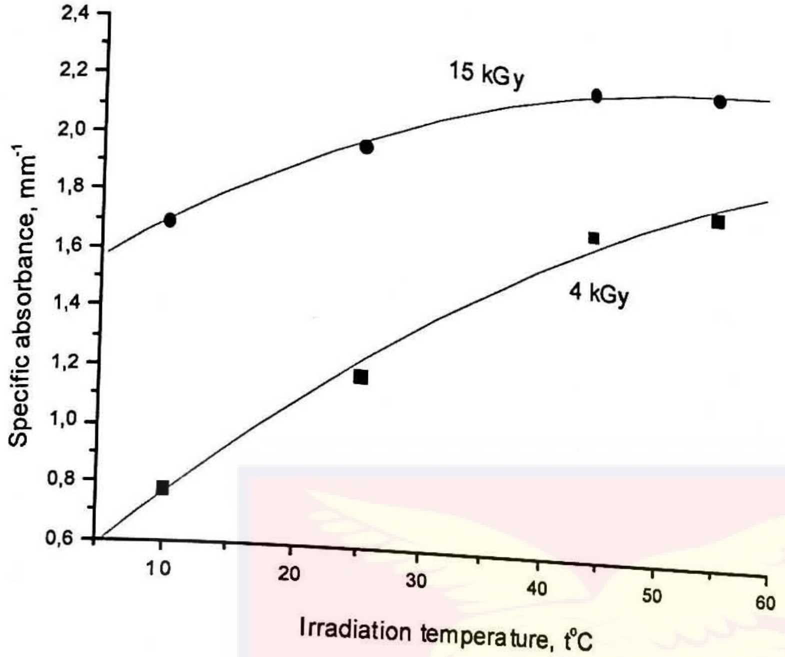


Fig. 49: Responses of films irradiated at different temperatures to doses of 4 and 15 kGy

Effect of humidity on the response of film

Film and dose	12 % rel. hum.	34 % rel. hum.	55 % rel. hum.	75 % rel. hum.
1 mmol dm^{-3} 5 kGy	1.35	1.36	2.05	2.71
1 mmol dm^{-3} 25 kGy	2.08	2.30	3.61	4.16
10 mmol dm^{-3} 5 kGy	1.04	1.28	2.25	2.62
10 mmol dm^{-3} *25 kGy*	4.91	5.07	6.02	6.44

Table 2: Effect of relative humidity on the response (specific absorbance values) of polyvinylalcohol-tetrazolium violet dosimeter films

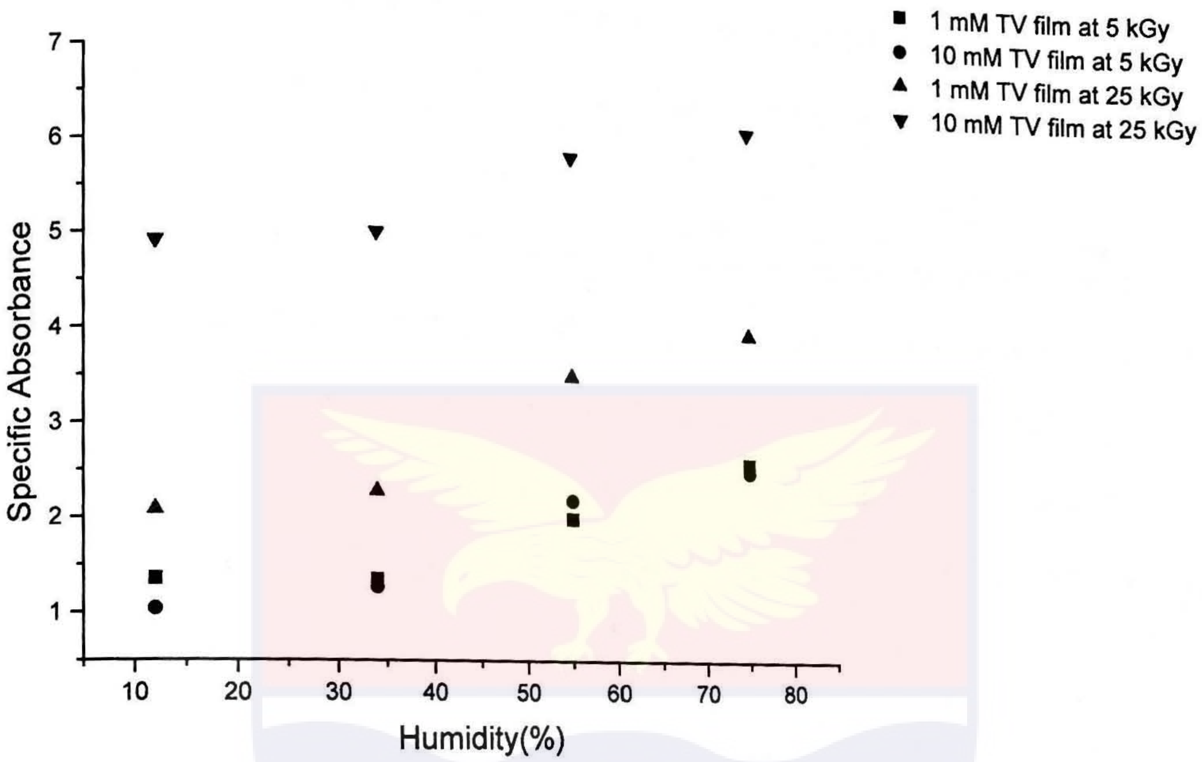


Fig. 50: **Performance of TV film against humidity during irradiation**

The influence of humidity on the response of the films are shown in fig. 50 with respect to the dose given and the concentration of the TV in the film. It is observed that the absorbance of any given film irradiated to a given dose increases with respect to humidity.

Applicability test of the TV – PVA film under industrial conditions

In order to establish the suitability and possible applicability of the TV - PVA film under actual radiation processing conditions, the dose response of the film was studied in industrial gamma and electron beam irradiation facilities. The films were irradiated in polystyrene calibration phantoms together with transfer standard dosimeters. Ethanol-monochlorobenzene dosimeter solution was used as transfer standard system in the case of gamma irradiation, while in the case of irradiation with electron accelerator it was polystyrene calorimeter.

In both cases, i.e. under gamma and electron irradiations similar dose response was observed in the dose range investigated. The irradiation temperature varied in both facilities depending on the dose; being between 30 °C and 45 °C in the gamma facility, while in the electron irradiation facility it was between 35 °C and 50 °C. The dose response as measured in the two facilities is shown on Fig. 51 and indicates the applicability of this dosimeter film under industrial conditions.

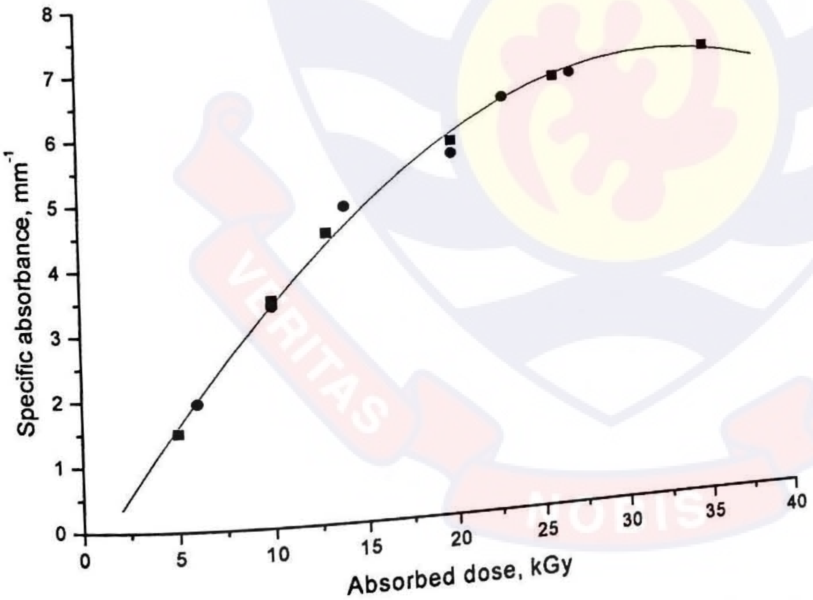


Fig. 51: Dose response of the 2 mmol dm^{-3} TV - PVA dosimeter film in industrial scale gamma (●) and electron (▪) irradiation facilities

CHAPTER 7

DISCUSSIONS

Discussions

From the observations of the dynamic and steady state investigations on the solutions and on the films or solid phase systems, the potential characteristics of tetrazolium violet for radiation processing dosimetry has been established as discussed below. The discussions also take into account the influence parameters like temperature, dose rate, concentration of the tetrazolium violet, humidity where applicable among others.

Electron pulse radiolysis investigations

The major reactive species available for reaction with the TV as solutes in aqueous solutions are the OH radical (oxidizing agent, G = 2.7), the solvated electron, e_{aq}^- (reducing agent, G = 2.7) and the H atom (reducing agent, G = 0.6). In acidic solutions e_{aq}^- is quickly transformed to H atom (G = 3.3). These species can be produced in a nanosecond using pulsed electron beam. The observations from the pulse radiolysis technique of the TV in aqueous solution under reducing and oxidizing conditions clarifies the reaction mechanisms that take place before the final formazan is formed.

Radiolysis of TV under reducing conditions

Under reducing conditions, where the oxidizing OH radicals is eliminated from the solution by N_2 saturation and the addition of tert-butanol, which also reacts with the OH radical to form the unreactive tert-butanol radical, solvated electron and H atom become the reducing reactive species present in the solution with the tert-butanol radical. The tert-butanol has however been proved to be rather inactive in reactions with tetrazolium salts. From the absorption spectrum taken 8 µs after the electron pulse in N_2 saturated tert-butanol containing solution (pH = 5.7) a strong absorption in the 300 nm – 600 nm region with a maximum at 340 nm and a smaller absorption peak at 420 nm followed by a decreasing absorption up to about 600 nm is observed as shown in Fig. 12. On a longer time scale, i.e. 0.8 ms after the electron pulse, the absorption at 340 nm and 420 nm gets significantly smaller, whilst the absorption observed 8 µs after the pulse in the 450 - 580 nm region is rather more pronounced. The behaviour of the solution is noted not to be significantly affected by increased pH (i.e. 6.7) except for the pronounced decrease of the two absorption peaks on a longer (ms) time scale.

It was observed generally that similar absorption bands occur in acidic, alkaline and neutral solutions at the shorter time scales i.e. 7 µs, after the electron pulse with maxima at 350 nm and 420 nm as well as on the longer time scales i.e. 0.8 ms, though with the increasing time the decrease of the absorption at 420 nm is much smaller with the acidic, while the absorption at around 450 nm become more significant. On the other hand significant differences occur both in the absorptions as well as in their ratios measured at 420 nm and in the 450 – 580 nm region, respectively. Much stronger absorption is observed in alkaline solutions than in neutral solution (Fig. 13). These observations indicate that the absorption at longer time scale (i.e. towards final product or formazan formation), there is an absorption increases from the acidic through the neutral to the alkaline solution when treated under the same conditions (Fig. 14).

In the acidic N_2 saturated solutions (pH = 3.2) not containing tert-butanol the fast formation and the significant decay on the longer time scale of the absorption at 350 nm was also observed with the fast formation of the "shoulder" at 410 nm although its decrease is much smaller on the ms time scale as well as the "build-up" of the absorption in the 450 nm – 550 nm region (Fig.15). This build-up may partly involve an OH adduct product and formazan.

The investigations with N_2 saturated aqueous – ethanolic (50 % - 50 %) TV solutions, similarly show as with the earlier observations, the fast formation (i.e. at 9 μs) of the absorption at 350 nm, showing decreased absorption on a longer time scale of 0.77 ms. The fast formation of the 420 nm absorption peak is also similar to the previous results, but in the present solution, there is no decrease of the absorption at longer times (0.34 ms). The absorption observed in the 450 nm – 550 nm wavelength range also forms quickly after the electron pulse and remains unchanged on longer time scale as well (Fig. 16).

Formation of the tetrazolinyl radical

From the observations made with dilute N_2-saturated tert-butanol containing neutral (pH = 5.7; pH = 6.7) and alkaline (pH = 10.8) solutions of TV salt, an intermediate product absorbing in the 300 – 500 nm region (maximum at 350 nm and another absorption peak at 420 nm) were observed immediately after the electron pulse (Figs. 12, 13, 17). This intermediate product if likened to reported observations of other tetrazolium salts (e.g. 2,3,5-triphenyl-tetrazolium chloride, 2-nitrophenyl-3.5-diphenyl-tetrazolium chloride, nitro blue tetrazolium chloride), - may be attributed to the electron adduct tetrazolinyl (tetrazolium) radical, where one of the rings of the TV is understood to have undergone one-electron reduction (Fig. 2).

$$TV^{+} + e_{aq}^{-} \xrightarrow{k} TV^{\cdot} \qquad (7.1)$$

The kinetics of this process can be described according to the following differential equation:

$$d[e_{aq}^{-}]/dt = - k[TV+]\,[e_{aq}^{-}] = - k'\,[e_{aq}^{-}] \qquad (7.2)$$

where

$$k\,[TV+]\,[e_{aq}^{-}] \cong k'\,[e_{aq}^{-}] \qquad (7.3)$$

since the tetrazolium violet concentration remains practically constant; thus

therefore

$$[e_{aq}^{-}] = [e_{aq}^{-}]_0\,(1 - e_{aq}^{-k't}) \qquad (7.4)$$

According to the investigations and based on the oscilloscope trace of the formation of the tetrazolium radical (Fig. 18), it was found that in the neutral and alkaline 0.1 mmol dm^{-3} TV solutions, this radical forms with a pseudo first order rate constant of 5 x 10^{9} – 2.3 x 10^{10} L mol^{-1} sec^{-1}. This value is close to the values published in literature or similar molecules (Kriminskaya et al., 1988; Lecheheb, 1984).

Again according to the investigations, the tetrazolium radical decays in a second-order process resulting in the final radiolysis product, the formazan, as discussed later. The decay of the tetrazolium radical is shown in Fig. 18. together with the fitting curve to calculate the second order rate constant, which was found to be $2k/\varepsilon_{350\ nm} = 1.2 \times 10^6$ cm s^{-1}.

The other absorption appearing at 420 nm also forms very fast and decays on a longer time scale in acidic and neutral solutions. In alkaline solutions, however, this absorbing species decays in a few tens of microseconds, but on a longer time scale its absorption become almost stable. It can therefore be assumed, that the absorption immediately after the electron pulse is also due to the tetrazolium radical, which decays after its formation, but on a longer time scale (i.e. hundreds of microseconds) the absorption is due to the build-up of a new product as explained below.

In N_2 saturated solutions without tert-butanol similar spectra with formation kinetics were observed in this wavelength range both in aqueous acidic (pH = 3.3, Fig. 15) and in neutral aqueous - ethanolic solutions (pH = 6.7, Fig. 16) like in the solutions containing tert-butanol. In the latter case, however, the absorption observed at 420 nm seems to be remaining even at 0.8 ms after the electron pulse.

In N_2 saturated tert-butanol containing neutral solutions (pH = 5.7 and 6.7) the broad absorption band which gradually appears in the 450 - 580 nm region on the hundreds of μs and ms time scale (Figs. 12 and 17) and appearing faster in tert-butanol containing alkaline solutions (Fig. 19), possibly representing the final formazan product, became much more significant with higher yield in the same solution (pH = 10.8) as seen in Fig. 20, where the spectra taken 10 μs and 0.77 ms after the electron pulse are compared.

In order to characterize the formation of these species the absorption spectra - taken at different times after the electron pulse in the same acidic and alkaline solutions - were compared (Figs. 12 and 19). It was found that the appearance of the species at around 450 nm and 530 nm are connected with the decrease of the absorbance of the tetrazolinyl radical at 350 nm. Both the decay of the tetrazolinyl radicals and the formation of the species absorbing in the 450 – 550 nm range were found to follow second-order kinetics. It is reasonable to assume, therefore, that the tetrazolinyl radicals disappear in self-termination reaction ($2k/\varepsilon_{350\ \mathrm{nm}} = 1.2 \times 10^6\ \mathrm{cm\ s^{-1}}$) resulting in the formation of monoformazan as suggested in the case of other tetrazolium compounds (Kriminskaya, 1988; Kovács et. al, 1999):

$$TV^{\bullet} + TV^{\bullet} \rightarrow TV^{+} + MF^{+} + H_2O \qquad (7.5)$$

The oscilloscope trace of the formation of the formazan final product is shown on Fig. 21 together with the result of the fitting procedure resulting in the second order rate constant for its formation ($k = 4 \times 10^9\ \mathrm{dm^3\ mol^{-1} sec^{-1}}$).

During the decay of the tetrazolium radical, the absorption of the formazan production already begins to appear at 420 nm on longer time scale and in alkaline solution or in aqueous-ethanolic solution it is even faster resulting in the observed absorption changes.

The formation kinetics of the species absorbing at 450 nm and 530 nm were found similar ($k_2 = 4 \times 10^9$ dm^3 $mol^{-1}sec^{-1}$) and of second order, which indicates that the absorption belongs to the same species, i.e. to the monoformazan, which is also in agreement with previous observations made in the pulse radiolysis studies of other tetrazolium salts (Kriminskaya, 1988; Kovács et. al, 1999; Altman, 1976).

The absorption spectrum of the monoformazan is similar at the different pH values studied, but the absorbance is much higher for pH = 10.8 than for pH = 5.7 due to the higher extinction coefficient (because of acid/base equilibrium) of this species at basic pH as reported earlier by Bielski (1980) whilst studying the radiolysis of the nitro blue tetrazolium; during which the extinction coefficients were published as 25400 and 12800 mol^{-1} dm^3 cm^{-1} in alkaline and neutral solutions.

Radiolysis of TV^+ under oxidative conditions

For solutions saturated with N_2O in which the hydrated electrons are captured by the nitrous oxide producing the oxidizing OH radicals, which then react with the solute. The absorption spectrum (Fig. 22) obtained shows similarities to the observations made with N_2 saturated solutions in the absence of tert-butanol, i.e. in both cases the absorbance builds up in a first-order process and decays according to second-order kinetics. Therefore it is assumed that this species is an OH-adduct, which forms in the addition reaction of OH radicals to one of the benzene rings of tetrazolium violet forming a cyclohexadienyl type radical. There are three different benzene rings in the molecule for the attack forming a variety of OH adducts.

The other broader absorption band observed in the 410 - 550 nm region forms also on the μs time-scale whose absorption remains even on ms time-scale is thus assumed to belong probably to a less reactive OH-adduct. Again as seen on Fig. 23 the spectra are similar for pH = 5.7 and pH = 10.7, but on the longer time scale corresponding to the final product, formazan, the absorption observed in the 410 – 550 nm region is somewhat stronger in alkaline solutions as explained before.

Radiolysis of TV in air saturated solutions

With the air saturated slightly acidic solutions (pH = 5.7) showing absorption maxima at 340 nm and at 420 nm which decreases fast and disappearing on the 0.78 ms time scale, it may be assumed that the two fast decreasing absorptions are related to the formation of the tetrazolium radical resulting in formazan formation (Fig. 24).

The other broad absorption band in the 440 – 600 nm region which begins to form a few μs after the pulse, but remains at 0.78 ms with two maxima at 440 nm and 480 nm may be attributed to the formazan formation under such conditions.

The absorption spectrum taken in air saturated solutions show similarities to the one taken in N_2O saturated solutions on ms time scale supporting the assumptions of the formation of OH-adducts (Fig. 25). As observed earlier, the absorption of the hydroxylated products and the formazan covers the same wavelength range as well.

Gamma radiolysis investigations

The potential dosimetric characteristics of tetrazolium violet for steady state radiolysis or gamma irradiation doses of aqueous, aqueous – alcoholic, alkaline and acidic solutions reveal, as discussed in the literature survey, the reduction of the salt in aqueous solutions mainly due to the reactions of the hydrated electron. In solutions containing primary or secondary alcohols, the α-hydroxyalkyl radical, which forms in the reaction of OH radicals and H atoms with the alcohol, also reduce the tetrazolium salt (Kriminskaya et al., 1984).

Radiolytic reactions of TV in aqueous solutions

The colour change associated with the irradiation of the neutral, air saturated TV solution from pale yellow to pink, depending on the dose given, becomes more intense with increasing dose as expected. The observation that the optical absorbance shows significant response after a dose of 250 Gy confirms the inhibitory effect of oxygen. The absorption spectrum of the unirradiated and irradiated 1 mM solutions to varying doses indicate the peak in the range between 530 – 560 nm (Fig. 12).

The optical absorption spectra of the unirradiated and irradiated air saturated, aqueous solutions of 1 mM TV (pH = 5.6), irradiated in the range of 1 kGy to 15 kGy, are shown in Fig. 26, It agrees with Fig 27 and the observations of Kovacs et al. (1999), Pikaev and Kriminskaya (1995) and Kovacs et al. (1996), that the radiation induced absorption in the visible spectrum with its maximum at around 516 nm and a shoulder at about 550 nm is due to the formazan formed by the radiation induced reduction of the TV salt.

The effect of TV concentration on the response of the TV solutions

It was observed (Fig. 28), that the absorbance of the solutions increase with increasing TV concentration for the same given dose of 5 kGy, i.e. the higher the concentration of the TV in the solution, the deeper the colour change for the same dose. This stems from the fact that the higher the concentration the greater the number of solute (i.e. particles) available per unit volume and therefore the higher the probability of interaction with the primary radiolytic products for the reduction process to take place. This makes higher concentration solutions of TV much more sensitive. However this also means that higher concentration solutions cannot be used for measurement of higher doses since the spectrophotometer readings or absorbance values get out of scale unless they are diluted. This effect was observed with 2 mM TV solutions, which could not be read for doses above 5 kGy unless diluted. The other significant observation made from the spectra is the shift of the absorbance peak towards longer wavelengths with increased concentration.

Effect of pH on TV solution response

For low pH (i.e. 3.34) the pale yellow solution turns brownish pink and precipitates even at 1 kGy. The unirradiated solution even precipitates under ordinary laboratory conditions after 24 hours, indicating that some reactions take place other than the radiation induced reduction process. Similarly for the high pH (i.e. 10.35) the solution becomes greenish black on irradiation and precipitating at 1 kGy while the almost colourless solution precipitates at 10 kGy. All these observations indicate that the non-neutral solution are not suitable for radiation processing control even though the spectrum of the optical absorbance is similar to the neutral solution upon irradiation. The fact that the acidic solutions become colourless after 10 kGy further disqualifies such preparation for process control dosimetry.

Radiolytic reaction of aqueous – alcoholic solution

In agreement with Altman and Butcher's (1973) observation, the resolution of the absorption peaks is better in solutions containing ethanol and for the same dose the absorbance is higher for the ethanol containing TV solutions, than for the neutral aqueous solutions.

One other observation made which is contrary to all published works is the production of greenish black precipitate even at 5 kGy in the aqueous - ethanol TV solution. However the spectrum from the irradiated solution is obtained after dissolving the precipitate in water or chloroform.

From the investigations of Kriminskaya et al (1983), the radiolytic reduction of tetrazolium salts (e.g. the 2,3,5 – triphenyl – tetrazolium chloride) is more pronounced in the presence of alcohols due to the additional action of the hydroxyalkyl radicals, formed from the alcohols which adds on to that of the hydrated electrons. However contrary to this observation the radiolysis of the aqueous solutions containing 50% by volume of t-buthanol in 1 mM TV aqueous solution changes colour from the usually pale yellow colour to light pink at 500 Gy, but with some precipitate. The colour change and precipitate becomes deeper with increased dose and begins to disappear becoming colourless at 15 kGy. The presence of the precipitate in addition to the usual colouration imply that quantitative estimation of dose cannot be achieved from this preparation (Fig. 30).

Effect of nitrogen saturation on irradiation of TV solution

The N_2 saturation significantly increases the response of the TV solutions with respect to doses as shown in Figures 30 – 32. This confirms the inhibiting effect of oxygen, which is eliminated or at least reduced in N_2 saturated solutions (Pikaev and Kriminskaya, 1998). The measured absorbance e.g. at 516 nm was 0.024 for the air saturated and 0.106 for the N_2 saturated solutions when the solutions were irradiated to 250 Gy. Similarly the absorbance at 516 nm was 1.283 and 1.75 for the air saturated and N_2 saturated respectively at a dose of 5 kGy.

Stability of irradiated TV solution after irradiation

The stability of the irradiated solution after irradiation, i.e. the stability of formazan formed, was investigated with 1 mM TV solution as shown in Fig. 33 The observation indicates that the irradiated solution is practically stable for at least 2 hours after the irradiation when the absorbance is only +1.5% of the value if taken immediately after irradiation. After 2 hours the error due to the absorbance increase may be unacceptable, reaching +20% of the initial value after 24 hrs (Fig. 33).

Dose rate effect on the response of irradiated TV solution

The effect of dose rate on the response of the 1 mM TV solution irradiated to the same dose revealed significant dose rate dependence. In the case of the solution irradiated to 5 kGy (Fig. 34) with two different dose rates, the absorbance was relatively higher for the dose rate of 1 kGy/h than for 15 kGy/h. At another instance, however, when the solutions were irradiated to 30 kGy (Fig. 35), the absorbance spectra (i.e. at 30 kGy) almost overlap for the dose rates of 1 kGy/h and 15 kGy/h, at the absorption peak of 506 nm. This implies that the response of the solution to irradiation also depends on the dose rate at which it is irradiated. At higher doses, i.e. above 30 kGy, the dose rate effect is not probably significant.

Effect of temperature on the absorbance of TV solution during readout

As seen in Fig. 36 and Table 1, the absorbance of the TV solutions during readout decreases from 10°C to 30°C but only slightly increase between 30°C and 60°C. These observations imply that temperature corrections are required for dose evaluations during routine use.

Dose response relationship of the TV solutions

The response effect of 0.5 mM, 1.0 mM and 2.0 mM TV concentrations gamma irradiation or formazan formation in aqueous air saturated solutions has established that higher concentrations give higher absorbance values for the same given dose. Additionally since low concentrations of TV imply fewer number of reactive TV particles per unit volume available for the reduction process, the maximum achievable dose is low (e.g. 750 Gy for 0.5 mM TV). The higher concentration TV solutions, however, tend to produce more formazan than what the readout spectrophotometer can measure at high absorbance values (i.e. it goes off scale at relatively low doses) e.g. the 2 mM TV solutions could not be read above 5 kGy without dilution. The high absorption of the radiolysis product (i.e. formazan) for high concentrations of TV may therefore require dilution of the irradiated solutions in order to get measurable absorption values for higher doses with the spectrophotometer. The 1 mM TV solution, however, could be studied beyond 15 kGy.

Figs. 37 and 38 represent the dose response relationship for the 1mM TV solution for doses up to 10 kGy and 50 kGy respectively at the absorption peak of 504 nm.

Dosimetry characteristics of the polyvinyl alcohol based TV film

The tetrazolium violet as a radiochromic dye containing polyvinyl alcohol (PVA) film was prepared as discussed in the experimental section. The films were characterized using mainly absorbance measurements and the colour changes in all cases was from colourless to violet depending on the dose delivered.

Characteristics of the PVA-TV film by evaluation of absorbance

The exposure of the PVA-TV films to direct laboratory lighting, direct and indirect sunlight as compared to the film without the TV show (Fig. 39 and Fig. 40) generally that the absorbance could be affected adversely but no absorption peaks in the studied wavelength range were observed.

Effect of TV concentration on the performance of the film

Similar to the observations made with the aqueous TV solutions, the colour of the film turns increasingly violet with increasing dose as expected. This is in agreement with the suggested reaction scheme, i.e. the formation of formazan. The response of the films on the TV concentration, dose rate and dose are shown in figs. 41 and 42 with the absorption maxima occurring at ~ 525 nm.

Similar to the solutions, the films containing 0.5 – 0.1 – 0.2 mM TV dye were found with the maximum measurable dose increasing with TV concentration, implying that a wider measurable dose range may be obtained by using higher concentrations of the solution in the preparation of the film. With higher concentrations of TV, the absorbance at the absorption peak increases for the same absorbed dose as compared with films containing lower concentrations of the TV. The absorption spectra of the 0.5 mM TV film (Fig. 43) show absorption peaks of higher absorbance for increasing dose up to 60 kGy. The spectrum of the 75 kGy irradiated film has a lower absorbance at its absorption peak than the 30 kGy irradiated film. This shows that at this dose all the tetrazolium violet had then been consumed through the reduction process and further reduction has reduced some of the formazan formed to hydrazine (Pikaev and Kriminskaya, 1988).

Fig. 44 shows a polynomial responset to the dose-at the peak absorbance at 525 nm for the 0.5 mM TV for doses up to 60 kGy.

The performance of TV films prepared from aqueous – ethanol solutions

The films prepared from aqueous – alcoholic solutions containing TV, showed significant increase in the measured absorbance at relatively low doses and the maximum measurable dose was 6 kGy. This implies that above 6 kGy, all the solute in the film may have been consumed and any further irradiation causes the formazan formed to be further reduced to hydrazine. The initial enhancement of the reduction process leading to the high absorption confirms the contribution of the α-hydroxyalkyl radicals to the reduction – which form in the reaction of OH radicals and H atoms with the alcohol (Kovacs et al, 1999).

Effect of pH on on the response of the TV films

The effect of pH on the performance of TV-PVA films are not different from what was observed for the solutions. In the case of the films produced from low pH (3.34) solutions, it was observed that they could not be used above 4 kGy (i.e. Fig. 47) while the TV films produced from the high pH (10.4) solutions showed no peaks even at 2 kGy (Fig. 48). They may be used only for very low dose applications.

Effect of temperature on the response of films

The irradiation temperature affects the readout or response of the film, as shown in Fig. 49, the specific absorbance increases with increasing temperature. Due to the non-linear response observed, the calibration of these dosimeter films is suggested to be carried out under actual irradiation conditions, i.e. in-plant calibration is recommended.

Effect of humidity on the absorbance of films

The increased humidity implies increased availability of water molecules in the film and hence increased radiolytic products to support the reduction process in the films. This possibly explains why for the same dose the sample irradiated in a more humid environment shows increased absorbance (Fig. 50, Table 1). Corrections against humidity would therefore have to be considered in routine use of the TVG film for radiation processing dosimetry.

Based on the response of the films in the relative humidity range applied, it can be noted that conditioning of the unirradiated films in the humidity range of 12 – 34 % improves its performance.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The growing use of ionising radiation in industry, medicine, agriculture, environmental technology and radiation processing in general calls for reliable and quality control dosimetry methods. To satisfy these requirements and particularly in radiation processing dosimetry in Ghana, the characteristics of tetrazolium violet both in solution (i.e. liquid) and in the solid phase (i.e. film) through the colour-changes associated with it as a radiochromic dye systems upon irradiation has been studied.

Electron pulse radiolysis investigations

The major reactive species available for reaction with solutes in aqueous solutions, the OH radical (oxidizing agent, G = 2.7), the solvated electron, e_{aq}^- (reducing agent, G = 2.7) and the H atom (reducing agent, G = 0.6) have been investigated. In acid solutions e_{aq}^- is quickly transformed to H atom (G = 3.3). The observations made from the pulse radiolysis technique of the TV in aqueous solution under reducing and oxidizing conditions clarifies the reaction mechanisms that take place before the final formazan is formed.

Under reducing conditions, where the oxidizing OH radicals is eliminated from the solution by N_2 saturation and the addition of tert-butanol, which also reacts with the OH radical to form the unreactive tert-butanol radical, solvated electron and H atom become the reducing reactive species present in the solution with the inactive tert-butanol radical. From the observations made an intermediate product absorbing in the 300 – 500 nm region (maximum at 350 nm and another absorption peak at 420 nm) which if likened to reported observations of other tetrazolium salts (e.g. 2, 3, 5-triphenyl-tetrazolium chloride, 2-nitrophenyl-3.5-diphenyl-tetrazolium chloride, nitro blue tetrazolium chloride) may be attributed to the electron adduct tetrazolinyl (tetrazolium) radical, where one of the rings of the TV undergoes one-electron reduction. According to the investigations and based on the oscilloscope trace of the formation of the tetrazolium radical, in the neutral and alkaline 0.1 mmol dm^{-3} TV solutions, the radical forms with a pseudo first order rate constant of $6 \times 10^9 - 2.3 \times 10^{10}$ L mol^{-1} sec^{-1} which is close to the values published in literature for similar molecules (Kriminskaya et al., 1988; Lecheheb, 1984). Again according to the investigations, the tetrazolium radical decays in a second-order process (i.e. $2k/\varepsilon_{350\ nm} = 1.2 \times 10^6$ cm s^{-1}.) resulting in the final radiolysis product the formazan.

From the appearance of the species at around 450 nm and 530 nm being connected with the decrease of the absorbance of the tetrazolinyl radical at 350 nm and the fact that both the decay of the tetrazolinyl radicals and the formation of the species absorbing in the 450 – 550 nm range were found to follow second-order kinetics it is reasonable to assume that the tetrazolinyl radicals disappear in self-termination reaction ($2k/\varepsilon_{350\ nm} = 1.2 \times 10^6$ cm s^{-1}) resulting in the formation of monoformazan as suggested in the case of other tetrazolium compounds (Kriminskaya, 1988; Kovács et. al, 1999):

$$TV^{\bullet} + TV^{\bullet} \rightarrow TV^{+} + MF^{+} + H_2O \qquad (8.1)$$

The oscilloscope trace of the formation of the formazan final product shows that the formation kinetics of the species absorbing at 450 nm and 530 nm were found similar ($k_2 = 4 \times 10^9\ dm^3\ mol^{-1} sec^{-1}$) and of second order, indicating that the absorption belongs to the same species, i.e. to the monoformazan, which is also in agreement with former observations made in the pulse radiolysis studies of other tetrazolium salts (Kriminskaya, 1988; Kovács et. al, 1999; Altman, 1976).

With solutions saturated with N_2O in which the hydrated electrons are captured by the nitrous oxide producing the oxidizing OH radicals, the absorption spectrum (Fig. 22) obtained shows similarities to the observations made with N_2 saturated solutions in the absence of tert-butanol, i.e. in both cases the absorbance builds up in a first-order process and decays according to second-order kinetics. Therefore it is assumed that this species is an OH-adduct, which forms in the addition reaction of OH radicals to one of the benzene rings of tetrazolium violet forming a cyclohexadienyl type radical.

With the air saturated slightly acidic solutions the absorption spectrum shows similarities to the one taken in N_2O saturated solutions on ms time scale supporting the assumptions of the formation of OH-adducts.

Investigation of solutions of TV

The investigations have confirmed that the two-electron reduction process of tetrazolium salts on their radiolytic decomposition to form coloured formazan depends on the nature of solvent used and the presence or absence of oxygen. For instance, the optical absorbance of the 1 mM solution shows significant response only after a dose of 250 Gy which confirms the inhibitory effect of oxygen which is significant at low doses whilst the maximum dose is 15 kGy in the wavelength between 530 – 560 nm. The yield of formazan was also found to be significantly lower in aerated alcoholic solutions compared to deaerated (e.g. N_2 saturated) solutions as reported earlier with other investigations. The concentration of formazan formed was found to be proportional to the initial concentration of the TV solution. However the optical absorbance could not be determined for such concentrations of formazan unless diluted some times 10 fold. For instance with 2 mM TV solution the optical absorbance could not be read for doses above 5kGy unless diluted.

The TV solutions systems have been found not to be suitable for high or low pH preparations. The neutral solutions do not precipitate which is contrary to all published works as compared with the production of greenish black precipitate even at 5 kGy for the ethanol TV solution. However the spectrum from the irradiated ethanolic solution is obtained after dissolving the precipitate in water or chloroform.

Distinctively the formation of formazan is enhanced under reduction conditions and inhibited under oxidative conditions. The absorbance of the irradiated films and aqueous TV systems were measured with UV spectrophotometer which is relatively a cheaper readout system and almost available at all facilities. The dosimetry characteristics of both the aqueous and film systems investigated reveal that the aqueous systems are not affected by environmental conditions as with the films. The useful dose range of both the liquid and solid system and the effect of dose rate, humidity, pH, irradiation temperature on the response of the TV system give interesting result.

From the observations made from the dynamic and steady state investigations on the solutions as well as the film or solid phase systems, the potential characteristics of tetrazolium violet for radiation processing dosimetry has been established as discussed below. The discussions also take into account the influence parameters like temperature, dose rate, concentration of the tetrazolium violet, humidity where applicable among others.

The colour changes associated with the irradiation of the neutral air saturated TV solutions from pale yellow to pink depending on the dose given, becomes deeper with increasing dose with its maximum occurring at around 516 nm and with a shoulder at about 550 nm. is due to the formazan formed by the radiation induced reduction of the TV.

High concentrations of the TV in solutions turn deeper in the colour changes for the same dose and may read off scale on the spectrophotometer. For instance the 2 mM TV aqueous solutions could not be read for doses above 5 kGy unless diluted. The pH of the prepared solution also affects the response of the TV, being suitable only for neutral solutions preferably with pH between 5 and 6. The acidic and basic aqueous solutions precipitate upon irradiation making those preparations unsuitable for dosimetry purposes.

As observed by Altman and Butcher's (1973) the resolution of the absorption peaks is better with aqueous - ethanol solution systems for the same dose and the absorbance is also higher than for the neutral aqueous solution. This would allow such preparations to be used for low dose measurements. N_2 saturation increases the response with respect to dose confirming the inhibitory effect of oxygen, which is eliminated by the N_2 saturated solutions (Pikaev and kriminskaya 1998). Again this allows low doses in the neighbourhood of 250 Gy to be measured.

Similarly the solutions of TV are relatively stable under conditions in the darkness but after irradiation the formazan formed is almost stable within the first 2 hours but increases significantly after 24 hours. Maximum corrections of 1.5% may be applied within the first 2 hours but as much as 20% would be required after 24 hours. The other factor which impacts on the formazan formation is the dose rate but not with any given trend. For instance at a dose of 5 kGy (i.e. Fig. 34), the absorbance was relatively higher for the 1 kGy/h than for the 15 kGy/h where as from Fig. 35 the absorbance spectra at 30 kGy almost overlap, for the dose rates of 1 kGy/h and 15 kGy/h, at the peak of 506 nm. This implies that both the dependence of the formazan formed on the dose rate is also influenced by the dose given. At higher doses above 30 kGy, the dose rate effect may not be significant.

The absorbance decreases from 10 °C to 30 °C but only slightly increase between 30 °C and 60 °C. The maximum absorbance occurs at 10 °C with the value of 1.683 for the 1 mMTV solution and at a wavelength of 516 nm at 25 °C whereas at 60 °C the absorbance is 1.405. These observations imply that temperature corrections are required for dose evaluations during routine use.

The effect of TV concentration of 0.5, 1.0 and 2.0 mM, on the dose or formazan formation in aqueous air saturated solutions proved that higher concentrations give higher absorbance values for the same given dose. However the higher concentration solutions tend to produce more formazan that the readout spectrophotometer goes off scale at relatively low doses (e.g. 2 mM TV solutions could not be read after 5 kGy) thus for high concentrations of TV dilution of the irradiated solutions may be required to get measurable absorption values for higher doses. However the 1 mM TV solution could be studied beyond 15 kGy.

Characteristics of the dosimeter film by evaluating its absorbance

The exposure of the prepared films to direct laboratory lighting, direct and indirect sunlight as compared to the film without the TV show that the film could be affected adversely and thus the prepared film must be kept in the dark.

The colour of the film turns violet upon irradiation in agreement with the reaction scheme for the reduction process leading to the formation of formazan. The factors affecting the response of the films are concentration, dose rate and dose dependent with the absorption maximum occurring at ~ 525 nm. The maximum dose increases with increasing concentration, implying that a wider measurable dose range may be obtained by using higher concentrations of the solution in the preparation of the film. The 0.5 mM TV film could be used up to 60 kGy.

The films prepared from aqueous – alcoholic solutions containing TV could be used up to a maximum dose of 6 kGy. This implies that after 6 kGy, all the solute in the film may have been consumed and any further irradiation causes the formazan formed to be further reduced to hydrazine. The effect of pH on the performance of TV-PVA produced films are not different from that observed for the solutions. For low pH prepared films, the maximum doses measurable is 4 kGy whilst the high pH produced films could only go up to 2 kGy. They may be used only for very low dose applications.

No significant change in absorbance measurements with respect to temperature variation from 25°C -60°C was observed during read out. This effect implies that the film can be read without correction when temperature variations occur. However due to the non-linear response observed for variations in irradiation temperature conditions, the calibration of these dosimeter films is suggested to be carried out under actual irradiation conditions, i.e. in-plant calibration is recommended.

With increased relative humidity an increase in absorbance for the same given dose was observed. The trend of this absorbance increase was similar for each solute concentration and each dose applied. Based on the response of the films in the relative humidity range applied it can be concluded that conditioning of the unirradiated film may be required or corrections against humidity would be required in routine use of the TV film for radiation processing dosimetry.

The stability of the dosimeter films was tested by measuring the absorbance of the irradiated films immediately after irradiation and then on a longer term. The irradiated films were kept after irradiation under normal laboratory conditions in dark. No significant difference (±3%; 1σ) in the measured absorbance values was observed both in the case of the gamma- and electron irradiated films even 5 months after irradiation. The post-irradiation stability of the TV-PVA film is another advantage for its routine application in radiation processing.

From the industrial applications, one observes that there is no significant difference in the response of the films with respect to gamma or electron beam irradiation as shown in Fig. 51. It is also significant to note that these comparisons were made with ethanol-chlorobenzene dosimeter as transfer standard system for the gamma irradiation and polystyrene calorimeter system for the electron beam irradiation. However further detailed investigations, in comparison with reference or transfer standard dosimeter systems, are needed to control all necessary influence parameters in its application to establish the possibilities and limitations in its usage.

Recommendations

It has been established from the investigations of this work that 2, 5-diphenyl-3-(1-naphthyl)-2H-tetrazolim chloride is a promising dosimetry system for radiation processing both as a liquid and as a radiochromic dye in Polyvinyl alcohol film.

It is however recommended that further investigations for confirmation and possible identification of other influence parameters be carried out as a test before finally embarking on its use as a routine dosimetry system for radiation processing dosimetry sysyem.

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