Development of New Chemical Dosimeters for Radiation Processing Applications

by

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Declaration

I, hereby declare that the investigation presented in the thesis has been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree/ diploma at this or any other Institution / University.

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Synopsis

Radiation processing is controlled application of energy of short wave length radiation of electromagnetic spectrum known as ionizing radiations and includes gamma rays, accelerated electrons and X-rays to have desired effect on the product (General aspects radiation dosimetry 2008). Some of the major objectives of radiation processing are

- Sterilization of medical and packaging products
- Phytosanitation to overcome quarantine barriers in fruits and vegetables
- Insect disinfestations of food products
- Inhibition of sprouting in tubers, bulbs and rhizomes
- Delay in ripening of fruits
- Enhancement in shelf life by destruction of spoilage microbes in foods
- Elimination of pathogens and parasites in foods
- Cross-linking and degradation of rubbers and polymers
- Colour enhancement of gemstones

The success of radiation processing depends to a large extent on the ability of the processor:

(a) To measure the absorbed dose delivered to the product (through reliable dosimetry);

(b) To determine the dose distribution patterns in the product package (through process qualification procedures);

(c) To control the routine radiation process (through controlled procedures).Radiation processing envisages the use of ionizing radiation (energetic charged particles such as electrons or energetic photons such as gamma rays and X-rays) to cause desirable change. (Atomic Energy (Control of irradtion of food) Rules 1996). The key element of such activities is inevitably a well characterized reliable dosimetry system that is traceable to recognized national and international standards. Only such dosimetry systems can help establish the required documentary evidence. There is continuous demand of radiation processing indicator systems to demarcate processed commodities. Presently imported polyvinyl chloride based patented indicators are available as radiation indicators; these indicators are sensitive to heat and light. At present there are no indigenously developed systems that are commercially available. For many years, different chemical combinations were tried but encouraging results were not obtained.

With this back drop, four systems are developed; the results obtained from the radiation chemical and other investigations have been described and compiled under different chapters of this thesis. A brief account of each chapter has been given below.

General Introduction

In the beginning, the motivation behind the research work on the dosimeter and radiation indicator systems has been explained. Since, this thesis deals with the study of four systems namely low dose FSX dosimeter, radiation indicator liquid, radiation indicator gel and radiation indicator label (film), therefore a brief preview of their background, optimum chemical composition, influencing parameters and an account of the radiation chemical investigations has been discussed. Dosimeter systems currently used in the industry are discussed in detail, with the importance of indigenously developed dose measurement systems. Besides, a concise description regarding the application of developed systems for radiation processing industry has been provided.

Experimental Techniques

A brief overview of the different experimental techniques used has been illustrated in this chapter. The working principle of Gamma Chambers (GC-900 and GC -1200) used as an radiation source has been explained. Optimization studies of reagents involved are discussed in detail. The optimization studies involved studies on concentration variation, effect of dose rate, effect of dose fractionation, time dependency study, reproducibility study, effect of pH and effect of stabilizers on pre and post irradiation stability. Standardization of gamma chambers were performed by secondary standard dosimeters [Alanine EPR (ASTM 51607 2002) and Fricke (ISO/ASTM 51026:2015 2015)] brief description of the dosimetry system is provided in the chapter. Principle of UV-Visible absorption spectrophotometer instrument that was used for carrying out absorption studies is also explained.

Development of Chemical Dosimeter for Low Dose Range

In this chapter, elaborate description of experiments carried out for development of low dose dosimeter is discussed. The chapter describes the general methodology and approach for dosimeter development and requirements for establishing it as a standard. Accurate measurement of low dose radiation in complex systems is of utmost importance in radiation biology and related areas [*International Atomic Energy Agency (IAEA), 2000*].

Sorbitol was used for radiolytic sensitization of ferrous ion based Fricke dosimeter. The advantages of using sorbitol are its ready availability and high water solubility. Owing to its dissolution at room temperature, possible errors those are involved in calculation of dose due to thermal oxidation of ferrous ions during preparation of the FBX dosimetric solution could be avoided in the proposed dosimeter (*Gupta, B.L., et al. 1978*). Here, sorbitol acts as radiolytic sensitizer for the oxidation of ferrous ion, and xylenol orange forms a 1:1 complex specifically with ferric ions. Thus, the analytical detection limit of ferric ions is enhanced compared to other systems. Final composition of the dosimetric solution is; 0.5 mol/m^3 xylenol orange, 10 mol/m^3 sorbitol and 0.2 mol/m^3 ferrous ion in 50 mol/m^3 sulfuric acid. Radiolytic sensitization in combination with analytical enhancement of the ferrous based system, allows us to measure radiation dose in the range of 0.05 Gy to12 Gy with ease and high reproducibility.

The optimum composition of FSX solution for use as low level dosimeter was established. The dose response is non-linear with second order polynomial fit. Less than 1% coefficient of variation was observed during dose reproducibility studies, suggesting its application in measuring low doses with high accuracy. The pre and post irradiation study suggests that the un-irradiated solution, stored in dark environment under refrigerated conditions in the temperature range 5 to 10^{o}C can be used up to one month for dose evaluation. However, irradiated solutions must be read on the day of irradiation, so as to minimize the post irradiation effect due to incomplete reactions. The dosimeter exhibits good reproducibility in terms of absorbance values with coefficient of variation within 1%. In conclusion, the study suggests that sorbitol can be used as a readily soluble radiolytic sensitizer in FSX dosimeter, which can be used for measuring low dose radiation with high reproducibility.

Development of Radiochromic dosimeter for Radiation Processing

Part I: Leuco-dye based Radiation Indicator Liquid

Fuchsin solutions appear coloured due to absorbance in visible region by its central quinoid structure—viologen —that are "decolorized" upon sulfonation of the dye at its central carbon atom by sulfurous acid or its conjugate base, bisulfate. This reaction disrupts the otherwise favored delocalized extended pi-electron system and resonance in the parent molecule. The further reaction of the Schiff reagent with aldehydes is complex with several research groups have reported multiple reaction products with model compounds. In the currently accepted mechanism, pararosaniline and bisulfite combine to yield the "decolorized" adduct with sulfonation at the central carbon. The free, uncharged aromatic amine groups thereafter react with the aldehyde being tested to form two aldimine groups. These groups have also been named for their discoverer as Schiff bases (azomethines), with the usual carbinolamine (hemiaminal) intermediate being formed and dehydrated en route to the Schiff base. These electrophilic aldimine groups then react with further bisulfite, and the Ar-NH-CH(R)-SO_3^-product (and other resonance-stabilized species in equilibrium with the product) gives rise to the magenta color of a positive test (Yongjie Li, Meiping Zhao, 2006).

As primary alcohols such as ethanol, are oxidized to aldehydes (Maria Antoniadou et.al. 2013) photocatalytically (UV), experiments were carried out to check radiocatalytic (high energy) feasibility of the reaction. Ethanol, ethylene glycol, ethyl acetate, glycerine were tested for feasibility in the above reaction mechanism. Solution of Schiff's reagent (pararosaniline-sulphite) and glycerol/ethanol, in acidic medium, when irradiated, displayed promising results. The unirradiated solution is colourless and develops magenta colour upon irradiation. The absorbance of the solution increases with increasing dose (colour development), measurement is however not possible as the complex formed upon irradiation adheres to the wall of optical cell.

In view of this, a new system was tested for its performance as radiation processing indicator.

Part II: Development of New Radiation Processing Indicator based on formation of Erythrosine and its application as Radiochromic Dosimeter

Erythrosine(2',4',5',7'-Tetraiodo-3',6'-dihydroxy-spiro[3H-isobenzofuran-1,9'-xanthen]-3-one disodium salt) is a derivative of fluorescein. Iodination of fluorescein using iodine in hot dilute acetic acid yields erythrosine. Many techniques are available for the commercial synthesis of erythrosine. Based on the literature, radiation chemical approach was tested. Here, iodination of fluorescein using iodide-iodate (*Yi Xie, Michael R, Mc Donald, Dale W. Margerum, 1999*) in bicarbonate medium is studied and is proposed to be used in radiation processing as indicator. The colour of the solution changes from yellow (unirradiated) to red (2kGy) through orange.

The optimum composition of radiation processing indicator solution was established. 10 mol/m^3 of bicarbonate concentration was found to stabilize the post irradiation absorbance. Effect of 5 mol/m^3 concentrations of both borax and molybdenum (catalysts) were also studied.

All absorbance measurements were carried out at 525 nm (λ_{max} of mono-iodofluorescein) to reduce the threshold of detection. The range of measurement for the bicarbonate based system is from 200 Gy-2000 Gy.

Borax and molybdenum compounds act as catalysts for iodination reactions. This fact was utilized to sensitize the bicarbonate based system. Iodide based systems are unstable due to thermal oxidation of iodide to iodine. Addition of known antioxidants to the iodide system do stabilize the system by lowering the oxidation of iodide (*Larry W. Luckett and Richard E. Stotler, 1980*), however, use of sulphite, bisulphate, thiosulphite totally change the dose response. Addition of sulphite increases the threshold dose of detection from 200 Gy to 2 kGy. Also it was found that the increase in absorbance is abrupt as compared to system without sulphite.Other antioxidants such as thiosulphite and bisulphate show similar response.

Two different dose rates, 10 Gy/min and 40 Gy/min were used to study the effect of dose rate on the radiation processing indicator system; however, no significant effect of dose rate was observed. Single dose was divided into two fractions and given with a time interval of 30 and 60 minutes. However variation observed is insignificant.

The study suggest that the radiation processing indicator liquid developed is extremely simple to prepare, made from relatively nontoxic chemicals, that are available easily. The system can be used as radiochromic dosimeter to estimate the amount of dose received by a product.

Development of Radiation Indicator Gels and Films for Radiation Processing

Part I: Radiation Processing Indicator Gel

In this chapter, conversion of the developed radiochromic radiation indicator liquid system into a non spillable shelf stable gel is described. 10 % polyvinyl alcohol solutions were made by heating polyvinyl alcohol in single distilled water at 70^{o} C for 4 hours with continuous stirring. The prepared solution is cooled to room temperature and kept undisturbed for 6-8 hrs. The clear supernatant liquid is carefully decanted and crosslinked using Borax (*Steven Spoljaric, ArtoSalminen, Nguyen Dang Luong, JukkaSeppälä, 2014*). The gel is fluorescent yellow in unirradiated form that changes to orange on receiving a dose of 5 kGy. On further irradiation to a dose of 10 kGy the gel turns into deep red.

The gel form is stable for more than 12 months with no visually observed change. Dose rate effect was not observed similar to that noticed in solution form. Post irradiation colour change is stable for more than 12 months. The colour developed upon receiving dose is irreversible. Gel form was found to have lesser temperature effect as compared to solution.

The study suggests that the radiation processing indicator gel is extremely simple to prepare, made from relatively nontoxic chemicals that are easily available. The gel type indicator starts to respond from 300 Gy assuming a bright orange colour that gradually deepens and changes to cherry red upon receiving a dose around 10 kGy. The gel has a shelf life of more than a year.

Part II: Gamma Radiation Processing Indicator Film

In this chapter, few radiation indicator labels (films) are developed for radiation processing applications. Four systems were tested for feasibility, results are discussed.

Fluorescein-Iodine system: Polyvinyl alcohol films of iodine iodate fluorescein system (radiation processing indicator) were cast but the radiation response of the films formed is in extremely high doses (> 50 kGy).

The Starch-Iodine test is used to test for the presence of starch (*Jacob A Rendleman Jr., 2003*). Iodine solution - iodine dissolved in an aqueous solution of potassium iodide - reacts with the starch, producing a purple-black colour. The colour can be detected visually with low concentrations of iodine (20 mM/m^{3}at 20 °C). In the iodide based radiation processing indicator system it was observed that iodine is formed upon irradiation of iodide-iodate solution in the pH range7-9.

Borax buffered Iodide-iodate-Polyvinyl alcohol solutions were prepared. To this solution starch solution in distilled water is added and the resultant solution was irradiated. The solution turns blue-black upon receiving gamma dose. The solution was transferred to flat trough and dried for two days. Translucent film formed was irradiated, however no colour change was observed.

Eosin formation based Radiation processing indicator films

Based on the studies conducted during iodide-iodate-fluorescein system and literature survey, following system was studied. Bromination of fluorescein leads to formation of eosin, many commercial methods are known in the field (*Sushil Kumar Singh and D.D.Agarwal., 2014*). It was found that fluorescein is brominated by bromide-bromate in the presence of the (free radicals) radiation. The colour of the solution (absorbance) changes from yellow to red on receiving radiation dose (*Robert Sjoback, Jan Nygren, Mikael Kubista, 1995*). The above solution was incorporated with polyvinyl alcohol and made into films. The films were irradiated to incremental dose. The films on irradiation develop colour from yellow to orange (1kGy) and finally to red (5 kGy). The films can be used as go-no go radiation processing indicators.

Conclusions and Perspectives

The last chapter concludes the thesis with brief discussion of applications of the developed systems. The radiation indicator liquid and gel can be used for radiation processing facilities and research students as replacement for radiation indicator to roughly estimate the dose received by adjoining product. The validation of radiation processing can be achieved. The developed colour is stable for months so any ambiguity on radiation processing can be resolved. The bromide based indicator label can be used to ascertain radiation processing of the adjoining product. Thus the industrial application of the systems is discussed along with further scope of work.

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Chapter 1 Introduction

1.1 General

Radiation forms an inseparable part of our lives. Broadly radiation is categorized into two forms, namely ionizing and non-ionizing radiation. Ionizing radiation is radiation with enough energy so that during an interaction with an atom, it can remove tightly bound electrons from the orbit of an atom, causing the atom to become charged or ionized. Ionizing radiation encompasses a large group right from cosmic radiation to X-rays. Ionizing radiations are classified into two categories (i) Directly ionizing and (ii) Indirectly ionizing radiation. Alpha and beta particles along with gamma and X-rays are directly ionizing radiation, while neutrons are indirectly ionizing type of radiation.

Near ultraviolet, visible light, infrared, microwave, radio waves, and low-frequency radio frequency (longwave) are all examples of non-ionizing radiation. By contrast, far ultraviolet light, X-rays, gamma-rays, and all particle radiation from radioactive decay are regarded as ionizing. Electromagnetic radiations of wavelength less than 100 A^o belong to the class of ionizing radiation.

Nuclear industry deals with ionizing radiation. The discovery of X-rays and radioactivity heralded the start of atomic and nuclear physics, and the race was on to understand more about the nature and properties of the radiations and atoms which emitted these. Whilst the intricacies of the atomic forces were being unraveled by the physicists, the penetrating property of the radiation was being used in the medicine to make photographs of broken bones, and the discipline of X-ray diagnosis was born. In medicine, radiation was first thought to be a panacea and was used to treat all sorts of ailments, often without success and sometimes with unfortunate consequences. In the meantime, the pioneers working with the radiation and radioactivity were learning, to their cost, that the penetrating radiation could damage biological tissue. The positive corollary of this was that tumors could be treated by radiation, leading to the birth of radiation therapy. Radiation was not a panacea, but there is no doubt, as exemplified by the thoroughly developed fields of X-ray diagnosis, radiation therapy and nuclear medicine, that its proper discriminate use has brought enduring benefit to the general health of the mankind.

Further with the discovery of nuclear fission, rapid development of atomic weapons and nuclear reactors started. Radioisotopes were separated as fission products from spent nuclear fuel. Energy emitted by radioisotopes was tested for its use in radiation processing. High energy radiations include alpha, beta, gamma, neutron beams, and beams of charged particles.

High energy radiation sources can be divided into three groups: those employing natural or artificial radioactive isotopes, those that employ some form of particle accelerator, and nuclear reactors.

With emerging nuclear industry, electronics industry was also developing at a rapid rate. High energy, high intensity electron accelerators were being developed for applications. Thus, in addition to gamma radiation sources, electron accelerators were made available. Accelerators allowed irradiating large amounts of material at a fast rate. Thus, with growing nuclear and electronic industry, material processing began to emerge in new ways. ^{60}Co (gamma rays) and electron accelerators are currently the most widely used radiation sources for commercial applications.

Depending on the nature and size of the object to be irradiated and penetration required, different types of radiation are used. The less penetrating radiations are used where surface irradiation is adequate. Neutrons and heavy charged particle radiation dislocate atoms in solids and induce activity therefore generally avoided unless demanded by application. In radiation energies greater than 10 MeV ion are avoided to prevent activation.

The penetration of radiation energy into material depends on the nature of radiation, energy of the incident radiation and the source-sample geometry. In radio therapy applications high energy radiation is used with the aim to irradiate deep situated tumors without delivering large dose to surrounding organs. The approach is applied to radiation processing.

High energy ionizing radiation produce similar chemical changes upon irradiation, proportion of chemical change depends on the rate at which energy is transferred. At some point all ionizing radiations transfer energy via charged particles. The charged particles act as primary radiation especially electrons and positive ions, secondary electrons in case of X-rays and gamma radiation, or protons or other ionizing radiation in case of neutrons. The linear rate of loss of energy by ionizing particle traversing through a medium is the Linear Energy Transfer of the radiation, $keV\mu m^{-1}$.^{60}Co gamma radiation have LET value of $0.2\ keV\mu m^{-1}$. The LET value increases with mass of ionizing particle with the penetration inversely proportional to LET.

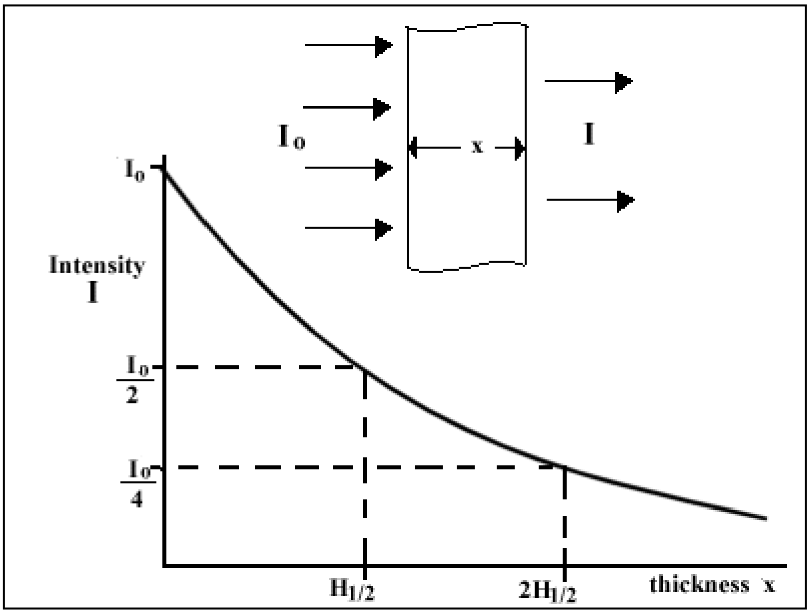


Figure 1.1: Attenuation of gamma radiation in medium

Gamma radiation cannot be completely absorbed, but only reduced in intensity, when passing through matter. When a narrow beam of mono-energetic photons, such as x-ray, γ rays, penetrates a surface of a material; it experiences a change in its intensity, owing to absorption or scattering that occur during the travel of the beam across the material. If mono-energetic gamma radiation attenuation measurement is made under conditions of good geometry, i.e. with a well-collimated, narrow beam of radiation, as shown in Figure 1.1, the expression of the intensity of the beam the long of an axis parallel to the direction that photons beam can be calculated as:

$I = I_o e^{-\mu\rho t}$ or $I = I_o e^{-\mu d}$

I = intensity after shielding

I_o = incident intensity, μ= mass absorption coefficient (cm^2/g),

d = thickness of absorber (g/cm^2)

ρ = density of absorber (g/cm^3), t = physical thickness of absorber (cm)

Interaction of ionizing radiation with matter

The radiation sources frequently used are ^{60}Co and electron beams generated by accelerators. The high energy γ gamma photons from radioactive sources produce energetic secondary electrons as they interact with the matter, so that both gamma and electron beam radiations produce similar chemical changes in the absorbing medium. Heavy charged particles such as α, traverse slowly and have a higher probability of interaction compared to high velocity electrons. Heavy charged particles produce tracks that are densely populated with ions and excited molecules, while electrons deposit much of their energy in isolated spurs with lesser concentration of ions and excited molecules.

Types of ionic and excited species for electron and heavy particles are same therefore chemical products of radiolysis are same in nature although differ in concentration. This difference is due to differential deposition of radiation energy i.e. LET effect.

For electron radiation, emission of electromagnetic radiation and inelastic and elastic collisions are most important interaction processes. Electrons radiate energy in the form of bremsstrahlung while moving close to nucleus (high atomic number). The bremsstrahlung energy is in the form of continuous X-ray spectrum starting from zero to energy of incident electron.

Electrons also loose energy through inelastic and elastic collisions, inelastic collisions being the dominant process that leads to ionization and excitation in the stopping material (Bethe and Ashkin 1953).

Unlike electrons and other charged particles electromagnetic radiation loses energy continuously through a large number of small energy transfers while traversing through medium. Photons loose relatively large amount of energy while interacting with matter however most of the photons traverse through the medium loosing infinitesimal energy or without any interaction. The interaction is dependent on incident photon energy and the atomic number of interaction medium. Depending on the interaction, gamma radiations are attenuated by a medium by three major processes, Photoelectric effect, Compton effect and the pair production. Coherent scattering and photonuclear reactions are some of other less significant interaction modes.

Coherent Scattering

A photon can be scattered with little loss of energy by several processes, majorly with atomic electrons. Rayleigh scattering is most probable at low photon energies (< 0.1 MeV) and in high Z materials. It is also known as coherent scattering as the effects combine coherently, that is, by the addition of amplitudes since there is a definite phase relationship between the incident and scattered photon. But as there is little difference in energy of incident and scattered photon, in addition to the small angular difference between them, its contribution to attenuation is neglected.

Photoelectric effect

Low energy photons interact predominantly by this effect, wherein entire energy of the photon is transferred to single atomic electron. The electron on receiving the energy ejects from its origin atom with energy that is left after overcoming its binding energy to the atom expressed by the following equation:

$E_e = E_0 + E_S$

$E_0$is the energy of incident photon, E_s is the binding energy of electron, and E_e is the difference between the photon energy and binding energy of electron in atom (Figure 1.2).

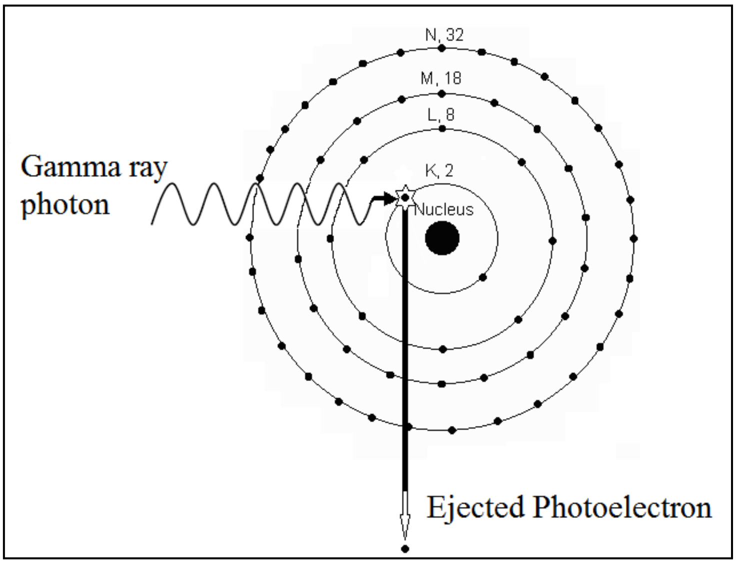


Figure 1.2: Photoelectric effect

At low photon energies the electrons are ejected predominantly at right angles to the direction of the incident photon, but as the photon energy increases the distribution shifts towards the forward direction. Energy and momentum are conserved by recoil of the remainder of the atom (effect observed with bound electrons)

Generally, most tightly bound electrons are ejected (K-shell). Interactions with K-shell contribute to 80 % of the photoelectric process with most other interactions at L-shell. The vacancy created by loss of electron is filled by lower energy orbital electron with emission of characteristic X-rays or low energy Auger electrons. Photoelectric interactions are most probable for high Z materials and low photon energies.

Compton Scattering

Compton scattering occurs between a photon and loosely bound or free electron, in the process the electron is accelerated and the photon deflects with reduced energy. The energy and momentum of the incident photon is shared between scattered photon and the electron. Compton scattering effects combine incoherently by the addition of the intensities of the effects since there is a random phase relationship between the incident and scattered radiation, hence Compton scattering is sometimes termed as incoherent scattering. Compton scattering Figure 1.3 predominates with the radiation energy between 30 keV to 20 MeV. From the equations for the conservation of energy and momentum it's possible to calculate the change in wavelength due to scattering is given by:

$$\Delta\lambda = \lambda' - \lambda = \frac{h}{m_e c}\left(1-\cos(\theta)\right)$$

λ is the initial wavelength of photon

λ' is the wavelength after scattering

h is planck's constant and its numerical value is 6.625×10^{-34} J . S

m_e is mass of electron (m_0),its numerical value is 9.11×10^{-31} kg

C is speed of light and its value is 3×10^{8} m/s

θ is the scattering angle of incident rays.

Here $\Delta\lambda = \lambda' - \lambda$. This term is known as Compton Shift.

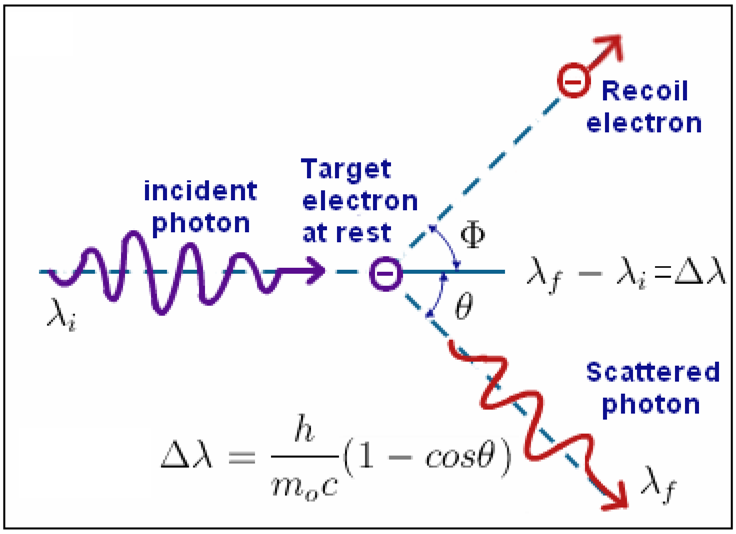


Figure 1.3: Compton Scattering

Pair production

Pair production Figure 1.4 involves the complete absorption of photons in the vicinity of an atomic nucleus or, less frequently, an electron with the formation of two particles, an electron and a positron. The incident photon energy is divided between kinetic energy of the electron and positron after spending the rest energies of for the two particles (m_ec^2). Momentum is shared by the recoiling nucleus. The positron after being thermalized in the medium combines with an electron to yield two 0.51 MeV gamma photons (annihilation radiation) in opposite directions. Pair production has threshold energy of 1.02 MeV ($2m_ec^2$).

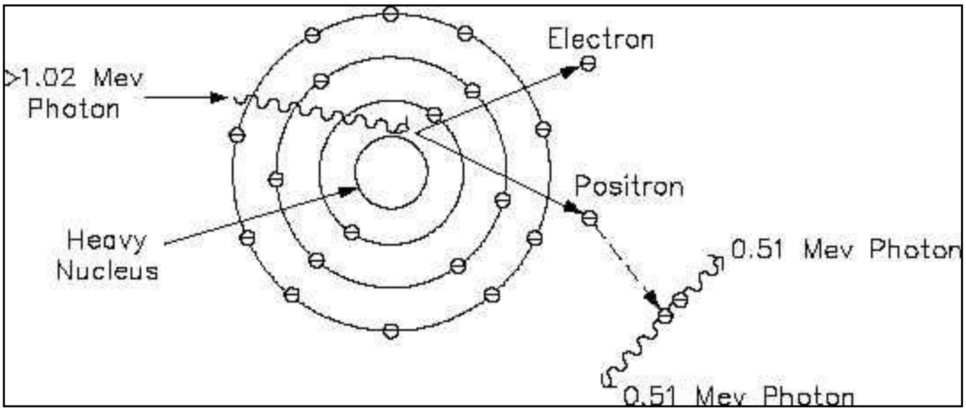


Figure 1.4: Pair production

Photonuclear reactions

Photonuclear reactions occur at 8 MeV for high Z materials and 10-20 MeV for low Z materials. Cross-sections for the interaction rises with increasing energies two to four times the binding energy, falling at higher and energies lower than binding energy of nuclear particles (neutrons and protons). The interaction probability of a medium energy photon is illustrated in Figure 1.5.

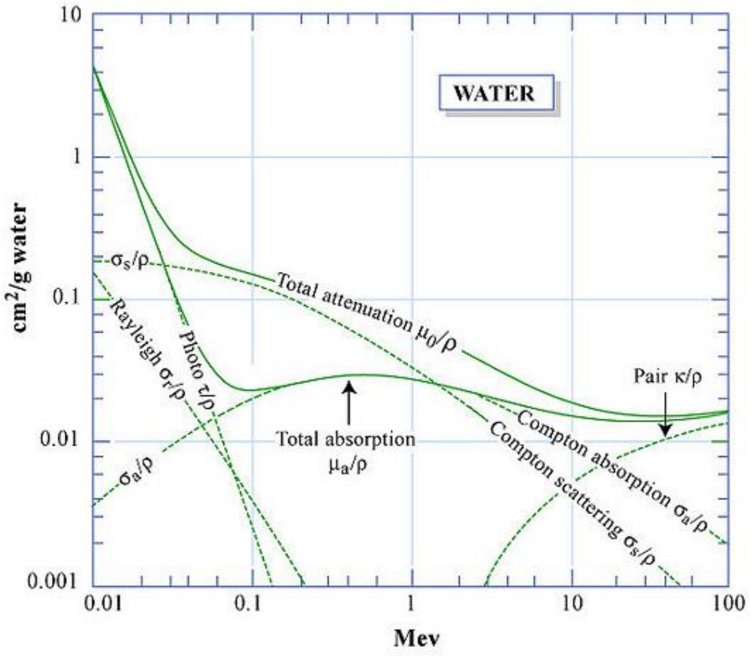


Figure 1.5: Total attenuation coefficient for water

Application of radiation in material processing was studied to harness the technology optimally. As knowledge of radiation chemistry and radiation biology was being improved, new applications of radiation processing were coined. High energy radiation was tested as initiator for polymerization, followed by cross linking of polymers. Other applications included the study of high energy on microbial world and its application in sterilization of medical products.

At present radiation processing is an emerging industry with applications growing steadily. Few applications are listed below.

a) Radiation sterilization of medical products, pharmaceuticals, cosmetics
b) Pathogen elimination in food and spices
c) Shelf life extension for perishable food
d) Polymer crosslinking and degradation
e) Flue gas treatment
f) Radiation polymerization
g) Mutation breeding.

Radiation sterilization is a wide term that applies to elimination of pathogenic microorganisms. Healthcare and the cosmetic industry are widely using the technology to process products in their final packaged state. Microorganisms are killed largely because of the damage caused to genetic material DNA. Radiation sterilization remains the best choice for sterilization, as it can be performed for heat sensitive compositions, without leaving any residues. 25 kGy is universally accepted dose for sterilization.

Preservation and pathogen elimination of food

The radiation-absorbed dose is the amount of energy, from any type of ionizing radiation, deposited in any medium (e.g., water, tissue, air). An absorbed dose of 1 rad means that 1 gram of material absorbed 100 ergs of energy (a small but measurable amount) as a result of exposure to radiation. The related international system unit is the gray (Gy), where 1 Gy is equivalent to 100 rad. The SI unit for absorbed dose is joules per kilogram (J kg^{-1}), which is given the special name gray (symbol, Gy).The absorbed dose rate per unit time is known as absorbed dose rate and has the unit Gy min^{-1} or Gy s^{-1}.The absorbed dose is directly proportional to the energy transferred to the irradiated material that is capable of producing chemical or physical change; it is determined both by the characteristics of the radiation field and the composition of the stopping material.

1.2 Radiation Chemistry

1.2.1 **Fundamental processes**

The subject of radiation chemistry deals with the chemical changes induced by high energy radiations, e.g. high energy photons (γ-rays, X-rays) and charged particles (electrons, protons, deuterons, α-particles). High energy neutrons can also induce chemical changes. Radiation chemistry, nearly a century old area of research and probably the basis of radiation biology (indirect effects) is still active in solving many day to day problems in industry, medicine and biology. In radiation chemistry the high energy photons and particles are not selective and may react with any molecule lying in their path, raising it to any one of the possible ionized and / or excited states. Thus a complex mixture of products is formed in contrast to relatively small number of products from a photochemical process. However, products may be formed selectively by appropriate manipulation of chemical reactions.

1.2.2 **Time scale of events after passage of radiation**

The overall process of producing chemical transformations starts with the bombardment of a system by radiation and terminates with the reestablishment of thermodynamic equilibrium. A sampling of the time scale of representative events is given below in Figure 1.6. Following energy deposition, the excited and charged species that are formed undergo the process of de-excitation, thermalisation, neutralization and solvation to form radiolytic species. Some of these species react among themselves at the site of production or may diffuse in space to become uniformly distributed before reaction. These radiolytic products viz., cations, anions, electrons, radicals and excited species are termed as primary species. The relative concentration can be different depending upon the physical state (solid, liquid and gas) of the medium, LET, energy of the radiation etc. (Aziz and Rodgers 1987)

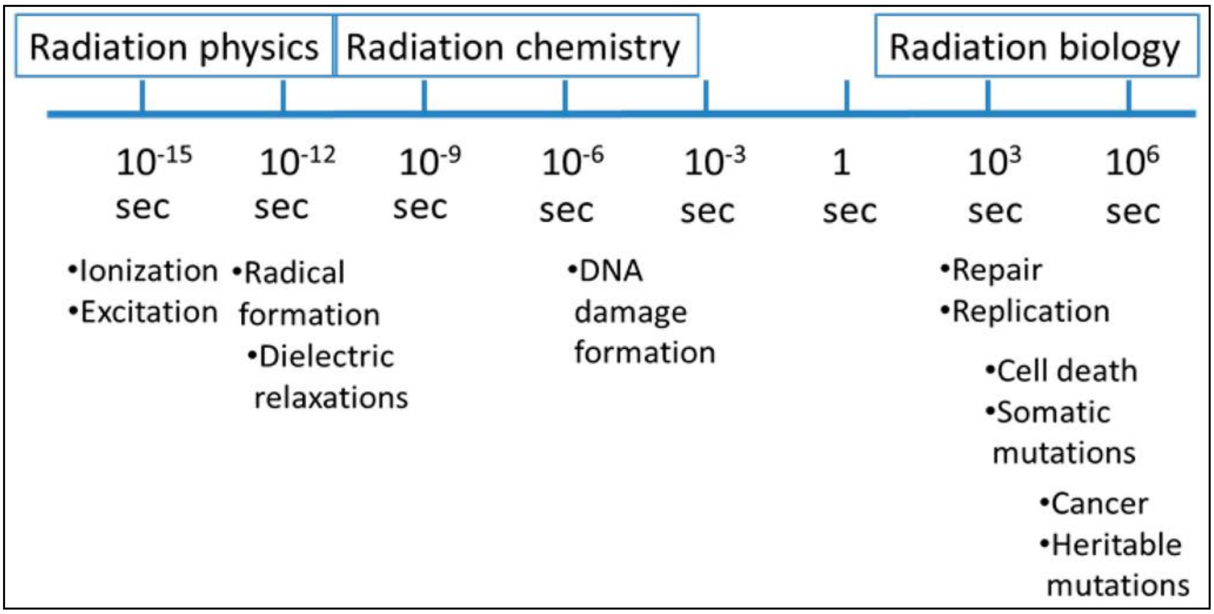


Figure 1.6: Approximate time scale of events after passage of radiation

The energetic electrons ejected as a consequence of primary ionization produce further ionizations and excitations. If the energy of these secondary electrons is relatively low, less than about 100 eV, their range in liquid or solid materials will be short and any secondary ionization that they produce will be situated close to the original ionization. A certain fraction of ions and excited species give rise to radical and molecular products. A small volume where a small number of excited and ionized spices, radicals and molecular products are grouped together in the medium is called a spur. The distance between the spurs will depend on LET of the radiation. The size of the spur is decided by the energy deposited from the high-energy radiation to the interacting molecule. If the secondary electron has energy between 100-500 eV it can travel more distance before it is reduced to sub excitation level. The reactive species are then distributed in a large volume called a blob. If the energy deposited is between 500-

5000 eV the secondary electron travels much more distance and a short track of ions and excited species is formed. Three different categories of track entities are considered according to the quantity of energy per interaction as given below:

Spur: energy deposited between 6-100 eV (1-4 ion-pair)

Blob: energy deposited between 100-500 eV (2-20 ion-pair)

Short track: energy deposited between 500-5 keV (20-200 ion-pair)

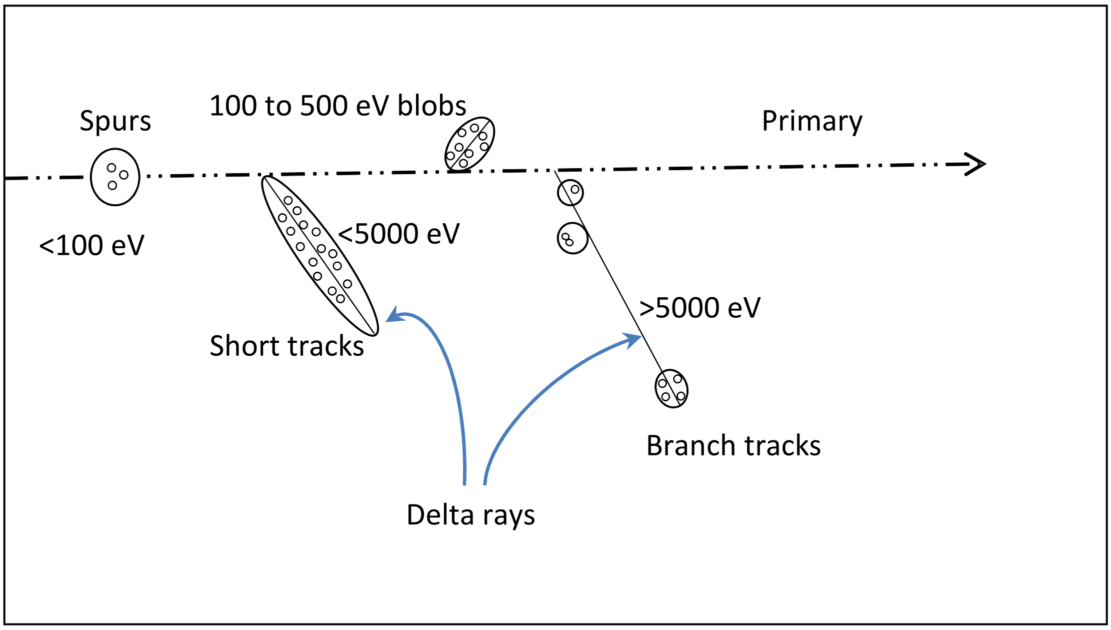


Figure 1.7: Distribution of ions and excited molecules in the track of a fast electron (not to scale)

The secondary electron having energy >5000 eV can act as a high-energy particle and a branch track will be formed. Thus the quantity of energy deposited determines whether an individual event will give rise to a spur or a larger group of ions and excited molecules. These demarcations are not rigid. The energy of the second electron is much less than that of the interacting high energy particle. The rate of energy transfer is much higher and the short and branch tracks will be more densely populated with the reactive species than the main track. This is illustrated in Figure 1.7.

The initial species viz. the ions and excited species, in general, are the same in a particular material regardless of the type or energy of the radiation responsible. After they are formed in the localized spurs, they diffuse in space with time. Uniform distribution in the medium takes around 10^{-7} s depending upon the medium. During this time of energy deposition to diffusion (10^{-16} to 10^{-7} s) the ions and excited species undergo many reactions like dissociation, thermalisation charge neutralization etc. The products at this stage are called the primary products and include cations, anions, electrons, radicals and excited states. All ionizing radiation will therefore give rise to qualitatively similar chemical effects in a particular medium. However, radiation of different types and energy will lose energy in matter at different rates, and consequently form tracks that may be densely or sparsely populated with the active species. The differences observed in the chemical effect of different radiations, differences in the quantities and proportions of the chemical product stem from the different densities of active species in the particle tracks. Expressions that reflect this changing density, such as specific ionization and linear energy transfer, are therefore useful in evaluating the overall chemical effect. Track effects of this sort are more important in the case of liquids, where the active species are hindered from moving apart by the proximity of other molecules, than in gases where they can move apart with relative ease. Thus, in gases the different types and energies of radiation do not give the markedly different yields of products. (Baxendale and Busi 1982)

1.2.3 **Radiation chemical yield**

Radiation chemical yield is a fundamental quantitative characteristic of any chemical transformation induced by ionizing radiation. Radiation chemical yields are described in terms of G values. Earlier G values were reported as the number of molecules of product formed X, as G(X), or of starting material Y changed G(-Y), per 100 eV energy absorbed. Radiation chemical yield has the same symbol G(X) or G(-Y) as the case may be and it is expressed as mol J^{-1} in SI units. It is the molar concentration of n, produced / changed for a known energy e is imparted to it.

$G (X) = n (X) / e$ mol J^{-1}

G-values in terms of number of species per 100eV can be converted to SI units by multiplying by 1.036×10^{-7} or in other words 1 mol J^{-1} = 9.649×10^{6} mol /100 eV.

The value of the radiation chemical yield may depend on the type of radiation and the chemical reactions involved. When the radiation-induced reaction is a chain reaction then the G value is high. For non-chain reactions it is not large. The value of G can be calculated if the absorbed dose and the concentration of the product being formed (or decomposed) are both known.

$G\ (\text{mol J}^{-1}) = n\ (\text{mol kg}^{-1}) / \text{Dose}\ (\text{J kg}^{-1})$

In actual practice the G value is found from kinetic curves, relating product concentration and absorbed dose. If the relationship is linear, the slope of the curve is the G value. If the initial experimental points show deviation from linearity, G is calculated by drawing a tangent to the curve from the point of origin.

1.2.4 **Free radicals**

Free radicals are atoms or molecules possessing one or more unpaired electrons that can take part in chemical bonding. The entities formed by loss or gain of an electron are free radicals as well as ions. The radical ions can give rise to neutral free radicals through unimolecular scission or bimolecular processes like disproportionation or protonation. Dissociation of excited molecules also gives rise to free radicals. They are formed at close proximity and in high concentrations initially. They react with another similar or dissimilar radical or diffuse into the bulk of the medium and generally react with the substrate. It is not possible to calculate the radiation chemical yield of radicals directly from absorbed dose. Pulse radiolysis and electron spin resonance techniques are the most important techniques for the detection, identification and measurement of free radicals formed.

The presence of an unpaired electron makes a radical unstable and extremely reactive. The reactivity (stability in the opposite sense) depends to a great extent upon its structure. Some examples are:

Reactive radicals: $H^\bullet$, $^\bullet OH$, $Cl^\bullet$, $^\bullet CH_3$, $^\bullet C_6H_5$

Stable radicals: $(CF_3)_2CF - {}^\bullet CF – CF (CF_3)_2$, 2,2-diphenyl-1-picrylhydrazyl (DDPH)

Reactive radicals have a short lifetime under normal reaction conditions. The stable radicals are generally formed from large molecules where the unpaired electron is distributed over a greater molecular volume. Generally, temperature and polar factors influence the reactivity of radicals. Free radicals react in such a manner that the odd electron is paired with a similar electron in another radical or eliminated by an electron transfer reaction. Thus they can be electron acceptors (oxidizing species) or electron donors (reducing species). The radical may react with another molecule forming a more stable radical.

The reactions of radicals can be divided into uni-molecular (rearrangement & dissociation) and bi-molecular (addition, abstraction, combination disproportionation, electron transfer).

1.2.4.1 **Rearrangement**

A reactive radical reaches a more stable structure by molecular rearrangement.

$(C_6H_5)_3C - CH_2^\bullet \rightarrow (C_6H_5)_2C^\bullet - CH_2 C_6H_5$

$Cl_3C\text{-}C^\bullet= \ \rightarrow \ Cl2C^\bullet\text{-} CCl=$

1.2.4.2 **Dissociation**

Radicals may dissociate into a smaller radical and an unsaturated compound

$CH_3CO^\bullet \rightarrow {}^\bullet CH_3 + CO$

$CH_3COO^\bullet \rightarrow {}^\bullet CH_3 + CO_2$

$Br_2CH\text{-}^{\bullet}CHBr \rightarrow Br^{\bullet} + BrCH = CHBr$

Many dissociation reactions are endothermic and increase in temperature favours this type of reactions.

1.2.4.3 **Addition**

Free radicals add to unsaturated compounds. This is a characteristic reaction of free radical. Another free radical is a product.

$Br^{\bullet} + R\text{-}CH = CH_2 \rightarrow R\text{-}^{\bullet}CH\text{-}CH_2Br$

$CH_2 = CH_2 + Br^{\bullet} \rightarrow {}^{\bullet}CH_2\text{-}CH_2Br$

Addition reactions are intermediate steps in radical initiated polymerization of unsaturated materials

$R^{\bullet} + AB \rightarrow {}^{\bullet}R\text{-}AB$

${}^{\bullet}R\text{-} AB + AB \rightarrow {}^{\bullet}R\text{-} AB\text{-}AB$

R is a radical and AB is a polymer.

1.2.4.4 **Abstraction**

These are the customary reaction of radicals with saturated organic compounds.

${}^{\bullet}OH + CH_3OH \rightarrow H_2O + {}^{\bullet}CH_2OH$

${}^{\bullet}H + CH_3I \rightarrow HI + {}^{\bullet}CH_3$

The species abstracted is generally a univalent atom, either hydrogen or halogen.

The radical formed is more stable than the attacking radical.

1.2.4.5 **Combination**

Combination reactions are generally favoured between two radicals. A stable molecule is formed.

$2\,{}^{\bullet}CH_3 \rightarrow C_2H_6$

${}^{\bullet}C_2H_5 + I^{\bullet} \rightarrow C_2H_4 + HI$

The energy liberated during combination can cause redissociation, if it is not lost through collisions.

1.2.4.6 **Disproportionation**

One of the atoms (normally Hydrogen) is transferred from one radical to another giving two stable molecules one of, which is unsaturated.

$2CH_3{}^{\bullet}CHOH \rightarrow CH_3CH_2OH + CH_3CHO$

${}^{\bullet}CH_3 + {}^{\bullet}C_2H_5 \rightarrow CH_4 + C_2H_4$

Disproportionation and combination often compete, but disproportionation is less common and depends upon conditions such as temperature, solvent etc.

1.2.4.7 **Electron Transfer**

Radicals are stabilized by electron transfer.

${}^{\bullet}OH + Fe^{2+} \rightarrow OH^{-} + Fe^{3+}$

${}^{\bullet}OH + Br^{-} \rightarrow OH^{-} + Br^{\bullet}$

The chemical changes brought about by ionizing radiation are mainly due to free radical reactions. Factors affecting radical reactions are the nature of the substrate (degree of unsaturation, substituents) reactivity of the newly formed radical, difference in the bond dissociation energies of the bonds being broken and formed, temperature, pH etc.

1.2.5 **Radiation Chemistry of water and aqueous solutions**

Water is the major and the most important component in chemical and biological systems. The study of the effects of ionizing radiation on aqueous solutions may serve as a model of the action of the radiation on living tissues. Water is used in nuclear reactors as moderator and coolant and thus comes in contact with reactor materials under radiation fields. Many processes involved in the production of atomic fuel and in the separation of the products of nuclear reactions are carried out in aqueous solutions. Therefore radiation chemical reactions taking place in water and aqueous solutions have been extensively investigated and fairly well understood now. Majority of the radiation-chemical studies is carried out in dilute aqueous solutions. ⇝ (curved arrow) in the report indicates radiation chemical change.

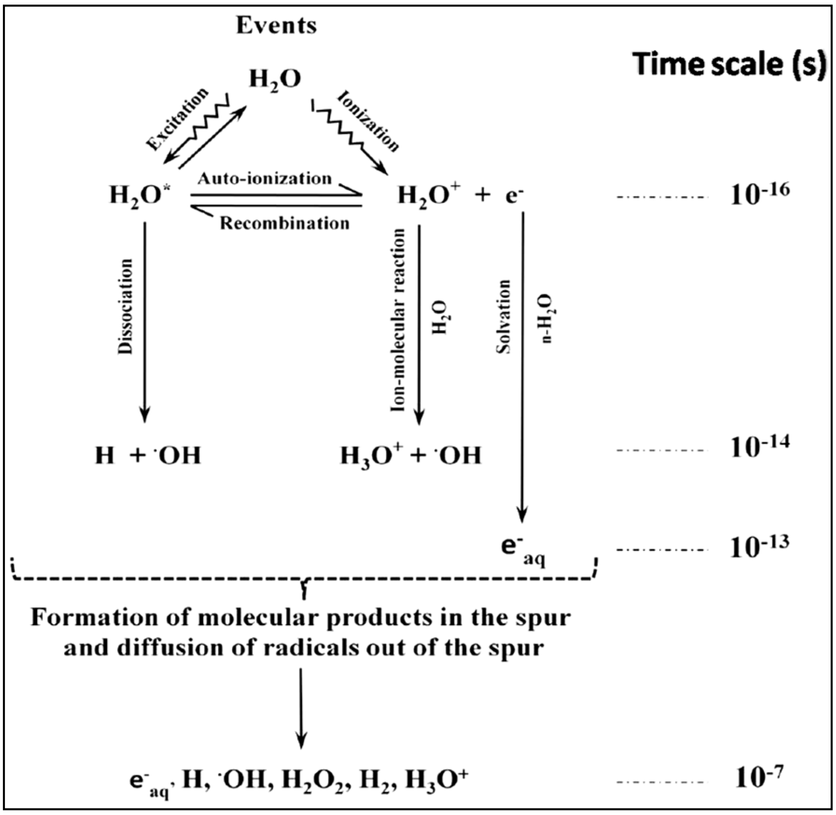


Figure 1.8: Time scale of events after passage of high energy radiation through water or aqueous medium

1.2.5.1 **Radiation Chemistry of water**

Water molecules are ionized by a charged particle directly or by photon or neutron indirectly. Some water molecules instead of being ionized may be excited to molecules of higher electronic states. This physical stage of interaction of the primary radiation with water happens within 10^{-14} s of passage of radiation.

$H_2O \rightsquigarrow H_2O^+, e^-, H_2O^*$

$H_2O^* + H_2O \rightarrow H_3O^+ + {}^{\bullet}OH + e^-$

$H_2O^+ + H_2O \rightarrow H_2O + {}^{\bullet}OH$

$H_2O^* \rightarrow [H^{\bullet} + {}^{\bullet}OH] \rightarrow H_2O$

The excited water molecule can dissociate or revert to the ground electronic state. Recombination of the electron with the +ve ion can also occur producing an excited water molecule. Studies conducted so far show that excited species do not play a significant role in radiation chemical changes in water. The electron liberated during ionization has sufficient energy to cause further ionizations and excitations of water molecules. When its energy falls below the ionization threshold of water, it loses the rest of the energy by vibrational and rotational excitations of water molecules. The water molecules orient to stabilize the excess negative charge in a cavity or void space. The electron thus gets solvated / hydrated due to the molecular dipoles rotating under the influence of the negative charge. This happens in less than 10^{-12} s after the initial ionization event. These hydrated electrons can last for microseconds at room temperature and they move and react like other chemical species.

$e^- + n\ H_2O \rightarrow e^-_{aq}$

In this physicochemical stage energy transfer, dissociation, ion-molecule reactions happen and complete within 10^{-12} s after the initial ionization event. The species e^-_{aq}, H, OH and H_3O^+ and any radical or molecular fragments resulting from dissociation of excited molecules are then in thermal equilibrium with the bulk medium and are localized in the spurs. This can be regarded as the beginning of chemical stage. They begin to diffuse a fraction of them encounter one another and react to form molecular or secondary radical products. The remainder escapes into the bulk of the medium and become homogeneously distributed. The reactions occurring while the spurs expand are completed by about 10^{-7} s and are given below:

$2e^-_{aq} \rightarrow H_2 + 2OH^-$

$e^-_{aq} + H^\bullet \rightarrow H_2 + OH^-$

$e^-_{aq} + {}^\bullet OH \rightarrow OH^-$

$e^-_{aq} + H_3O^+ \rightarrow H^\bullet + H_2O$

$2H^\bullet \rightarrow H_2$

$H^\bullet + {}^\bullet OH \rightarrow H_2O$

$2{}^\bullet OH \rightarrow H_2O_2$

${}^\bullet OH + H_2O_2 \rightarrow H_2O + HO_2^\bullet$

$2HO_2^\bullet \rightarrow H_2O_2 + O_2$

$H_3O^+ + OH^- \rightarrow 2H_2O$

Hence after about 10^{-7} s, e^-_{aq}, ${}^\bullet OH$, ${}^\bullet H$, H_2, H_2O_2, ${}^\bullet HO_2$ and H_3O^+, together known as primary species, are homogeneously distributed in water.

H_2O ^^^^^^-> e^-_{aq}, ${}^\bullet H$, ${}^\bullet OH$, ${}^\bullet HO_2$, H_2O_2, H_2, H_3O^+

The material balance equations are:

$G(-H_2O) = 2G(H_2) + G({}^\bullet H) + G(e^-_{aq}) - G({}^\bullet HO_2)$

$= 2G(H_2O_2) + G(OH) + G(HO)$

for low LET radiations, where HO_2 is negligible

$G(-H_2O) = 2G(H_2) + G({}^\bullet H) + G(e^-_{aq})$

$= 2G(H_2O_2) + G({}^\bullet OH) + G({}^\bullet HO_2)$

e^-_{aq}, ${}^\bullet H$, ${}^\bullet OH$ and ${}^\bullet HO_2$, are known as radical products and H_2 and H_2O_2, molecular products. These are often subdivided into reducing radicals (e^-_{aq} and ${}^\bullet H$) and oxidizing products (${}^\bullet OH$, ${}^\bullet HO_2$ and H_2O_2) since the two groups tend to bring about reduction and oxidation of solutes respectively. Molecular hydrogen is relatively inert and readily escapes. If retained in the solution (the system in closed condition) it can react with the hydroxyl radical.

$H_2 + {}^\bullet OH \rightarrow H_2O + H^\bullet$

Primary species yields can be determined indirectly by measuring products formed in the reaction of molecular or radical products with suitable solutes. The detailed radiolysis mechanism must be known for the yield calculations. Individual yields are derived algebraically. Pulse radiolysis technique is used to measure radical yields directly.

Water generally makes up the greater part of an aqueous system and acquires a correspondingly large fraction of the absorbed energy, chemical changes to the solutes occur when solutes react with the products of water radiolysis (${}^\bullet H$, e^-_{aq}, ${}^\bullet OH$, ${}^\bullet HO_2$, H_2O_2 etc.). This is known as the indirect effect on substances in aqueous solutions. At higher solute concentration direct action may be significant, solutes reacting with the initial products of energy deposition, the presolvated electron and H_2O^+. The direct effect is very difficult to investigate separately from indirect effect.

1.2.5.1.1 Properties of the primary products

1.2.5.1.2 Hydrated electron

e^-_{aq} has an intense absorption band. Reactions of e^-_{aq} with solutes are well studied by pulse radiolysis combined with kinetic spectrophotometry. It can be regarded as an electron trapped by a small group of water molecules, oriented as a result of the electron's presence. The reactions with solutes are generally very fast. It is suggested that e^-_{aq} can move the trap to solute without displacing the intervening molecules e^-_{aq} reactions are single electron transfer processes.

$e^-_{aq} + S^n \rightarrow S^{n-1}$

Where n is the charge (+, 0 or -) on the solute.

$e^-_{aq} + Cu^{2+} \rightarrow Cu^+$

$e^{-}_{aq} + H_3O^{+} \rightarrow {}^{\bullet}H + H_2O$

$e^{-}_{aq} + H_2O \rightarrow {}^{\bullet}H + OH^{-}$

$e^{-}_{aq} + H_2O_2 \rightarrow OH^{-} + {}^{\bullet}OH$

$e^{-}_{aq} + H_2S \rightarrow HS^{-} + H \rightarrow S^{-} + H_2$

$e^{-}_{aq} + {}^{\bullet}OH \rightarrow OH^{-}$

$e^{-}_{aq} + O_2 \rightarrow O_2^{-}$

In presence of water molecules

$e^{-}_{aq} + N_2O \rightarrow N_2O^{-} \rightarrow N_2 + OH^{-} + {}^{\bullet}OH$

$e^{-}_{aq} + CO \rightarrow CO^{-} \rightarrow OH^{-} + HCO$

e^{-}_{aq} acts as a nucleophilic reagent with organic compounds.

1.2.5.1.3 Hydrogen atoms

The H atom or radical is a slightly less powerful reducing agent than the hydrated electron. It is the major reducing species in acid media. In neutral and alkaline solutions, the reactions of H atom are not important. In alkaline solutions it reacts with OH^{-} to form a hydrated electron.

$H^{\bullet} + OH^{-} \rightarrow e^{-}_{aq} + H_2O$

It reduces cations like Cu^{++}

$H^{\bullet} + Cu^{2+} \rightarrow H^{+} + Cu^{+}$

In some cases H radicals can also react as an oxidant.

$H^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + H^{-} + H^{+} \rightarrow Fe^{3+} + H_2$

With saturated organic compounds, it usually abstracts hydrogen atom.

$H^{\bullet} + CH_3OH \rightarrow H_2 + {}^{\bullet}CH_2OH$

It also adds to unsaturated and aromatic compounds.

$H^{\bullet} + CH_2 = CH_2 \rightarrow CH_3 - {}^{\bullet}CH_2$

$H^{\bullet} + C_6H_6 \rightarrow {}^{\bullet}C_6H_7$

$H^{\bullet} + C_6H_5COOH \rightarrow {}^{\bullet}C_6H_5(H)COOH$

Abstraction of H atom from a -CH or $-CH_2$ group is easier as compared to $-CH_3$ group. Also H atom in the alpha position to a -COOH or -OH group is more susceptible to abstraction.

It adds to species having impaired electrons.

$H^{\bullet} + {}^{\bullet}OH \rightarrow H_2O$

$H^{\bullet} + O_2 \rightarrow {}^{\bullet}HO_2$

H atoms and hydrated electrons differ in their reaction with many organic compounds, H atom generally abstracting hydrogen to give molecular hydrogen, while the e^{-}_{aq} reacts to give other products.

1.2.5.1.4 Hydroxyl radical

OH radical generally behaves as an oxidizing agent with inorganic solutes. The reaction can be represented as a simple electron transfer process.

${}^{\bullet}OH + S^{n} \rightarrow S^{n+1} + OH^{-}$

S is the solute ion (+ve or -ve)

${}^{\bullet}OH + Fe^{2+} \rightarrow OH^{-} + Fe^{3+}$

${}^{\bullet}OH + CO_3^{2-} \rightarrow OH^{-} + CO_3^{-}$

Addition reactions occur with radicals.

$H^{\bullet} + {}^{\bullet}OH \rightarrow H_2O$

${}^{\bullet}OH + HO_2 \rightarrow H_2O + O_2$

OH as such does not add to oxygen.

Unsaturated organic compounds or aromatic systems undergo addition reactions.

$^{\bullet}OH + CH_2 = CH_2 \rightarrow HOCH_2CH_2^{\bullet}$

$^{\bullet}OH + C_6H_6 \rightarrow {}^{\bullet}C_6H_6OH$

Saturated organic compounds undergo abstraction reaction.

$^{\bullet}OH + CH_3COCH_3 \rightarrow H_2O + {}^{\bullet}CH_2COCH_3$

In strongly basic solutions (pH > 12) OH is converted to oxidizing O^-radical anions:

$^{\bullet}OH + OH^- \rightarrow O^- + H_2O$

O^- reacts with O_2 forming ozonide ion

$O^- + O_2 \rightarrow O_3^-$

O^- is not as reactive as OH radical

$O^-$is nucleophile whereas OH is an electrophile.

1.2.5.1.5 Perhydroxyl radical (•HO_2)

The perhydroxyl radical HO_2 and its anion, the superoxide ion ($^{\bullet}O_2^-$) are not significant with low LET radiation and play a minor role in the radiolysis of oxygen free solutions. They become important when oxygenated systems are irradiated because they are formed from reactions of other free radicals with oxygen. H atom readily adds to free radicals to form peroxy radicals.

$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet}$

$e^-_{aq} + O_2 \rightarrow {}^{\bullet}O_2^-$

$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$

$^{\bullet}H + O_2 \rightarrow HO_2^{\bullet}$

$HO_2^{\bullet}$is predominant below about pH 4.5 while O_2^- predominates above about pH 5. Perhydroxyl radicals act as oxidising or reducing agents depending on the solute. Ferrous ion, which is readily oxidised, is converted to ferric ion by reaction with $HO_2^{\bullet}$

$HO_2^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + HO_2^-$

$HO_2^{\bullet} + NO \rightarrow {}^{\bullet}OH + NO_2$

while ceric ion, which is a strong oxidising agent, is reduced to cerous ion.

$HO_2^{\bullet}$ is a stronger oxidising agent than ${}^{\bullet}O_2^-$.

$HO_2^{\bullet} + Ce^{4+} \rightarrow H^+ + Ce^{3+} + O_2$

Disproportionation of two peroxy radicals gives peroxide with the release of oxygen.

$2\ HO_2^{\bullet} \rightarrow H_2O_2 + O_2$

While the fundamental ionization processes are similar in all systems, properties of the medium such as phase, polarity and composition can greatly affect the chemistry. In all systems we need to understand what chemical species are formed, how they are dispersed spatially and what reactions can occur.

1.2.5.1.6 LET Effect

The linear density of events along the track is known as linear energy transfer (LET) and is expressed as keV/μ of track in the medium. The value of LET increases with the square of the charge on the particle and decreases as its speed increases. LET increases as the particle slows down towards the end of the track. So, mean values are generally taken. The average LET values for different radiations in water are given in Table 1.1. Energy deposited in short tracks, blobs and spurs for ^{60}Co gamma radiation are approximately 25%, 11% and 64% respectively. The same for ^{3}H β radiation is 74%, 8% and 18% respectively. Deposition of more energy leads to production of more active species. When the concentration of active species is higher, they are likely to interact with each other than reacting with molecules in the medium. These types of interactions lead to change in concentration of active species available for reaction with the medium and affect the final product yields. Ionizing radiations are classified as of low, intermediate, or high LET radiations depending on the LET value falling below , lying between, or exceeding respectively.

High LET favors reactions between radicals in tracks. An increase in the proportion of inter-radical reactions increases the proportionation of molecular products at the expense of radical yields. High LET favors reactions between radicals in tracks. An increase in the proportion of inter-radical reactions increases the proportionation of molecular products at the expense of radical yields.

Table 1.1: LET values in water

Radiation	KeV/μm
^{60}Co Gammas	0.23
22 Mv X rays	0.19
2 MeV electrons	0.20
200 kV X rays	1.7
^{3}H β	4.7
50 kV X rays	6.3
5.3 MeV α	43

1.2.5.1.7 Dose-rate Effect

The dose-rate is the ionizing radiation energy absorbed in unit time by unit mass of the irradiated substance. The unit is Gy time^{-1}. The dose-rates generally employed in radiation chemical studies using gamma rays are relatively low and of the order of a few Gy s^{-1}. At such values, the tracks of ionizing particles are at considerable distances from each other. Therefore, radicals diffusing out of the reaction zone of one track terminate their reactions completely before reaching the neighboring track. But if we irradiate water or a dilute aqueous solution by e- or gamma rays at a very high dose rate, many ionizing particles pass through unit area of the irradiated system at the same time, the tracks will be situated relatively near to each other. Intra track reactions are practically absent. However, The reaction zones of the neighbouring tracks will overlap and such overlap of tracks increases the probability of radical recombination reactions. Radical substrate reactions compete with reactions between pairs of radicals. If such competition occurs and the product yields are different for the radical substrate and radical reactions then radiolytic yield of product will be dependent upon the absorbed dose rate. Products characteristic of the radical reaction(s) will become more important as the absorbed dose rate is increased. High dose rates favors inter radical reactions in the system as a whole because of the high radical concentrations in the bulk of the medium. Dose rate effects are very predominant wherever chain reactions occur. In the absence of a chain reaction, very high dose rates may be necessary to produce significant radical concentration to get observable effects.

1.2.5.1.8 Effect of gaseous solutes

Radiolytic reactions are affected by the presence of dissolved gases like oxygen, nitrous oxide, hydrogen, argon etc. Oxygen plays an important role in radiation chemical reactions. The concentration of dissolved oxygen in air and oxygen saturated solutions are of the order of 0.25 mol m^{-3} and 3.0 mol m^{-3} respectively. Free radicals readily add to oxygen forming peroxy radicals.

$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet}$

$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$

$HO_2^{\bullet}$ and $RO_2^{\bullet}$ are not as reactive as $H^{\bullet}$ and $R^{\bullet}$

Peroxy radicals abstract hydrogen atom from organic molecules forming a hydroperoxide (ROOH).

$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$

Both forms of the radical are inert toward organic compounds unless these contain a relatively weakly bonded hydrogen atom.

ROOH is called a hydroperoxide and is not very stable.

$ROO^\bullet$can undergo various types of radical reactions as given below.

$2\ ROO^\bullet \rightarrow R\text{-}O\text{-}O\text{-}R + O_2$ (disproportionation)

$ROO^\bullet \rightarrow 2RO^\bullet + O_2$ (combination)

$ROO^\bullet + R^\bullet \rightarrow 2RO^\bullet$

$Fe^{2+} + ROO^\bullet + H^+ \rightarrow Fe^{3+} + ROOH$ (oxidation)

The above reactions continue to react slowly long after they have been formed. Radical reactions carried out in presence of oxygen, show delayed effects.Organic peroxyl radicals form HO_2 or O_2^- through bimolecular decay or reactions with organic substrates. The O_2^- may rise to relatively high steady-state concentrations. The deleterious effects of oxygen to the living cell (O_2 stress) are thought to be largely due to the formation of O_2^- and its subsequent reactions with transition metal ions. O_2^- is also formed in living cells through enzymatic reactions. It has a comparatively long lifetime and the slow reactions are of biological importance. Formation of peroxides and hydroperoxides, which are relatively stable molecules, may lead to slow oxidation. In Fricke and FBX dosimeters, reactions of radiation produced radicals are completed within a few milliseconds. But the peroxide reactions continue for several minutes following irradiation.

When water, saturated with nitrous oxide is irradiated, 10% of the radicals reacting with nitrous oxide are hydrogen atoms and the rest the hydrated electron. H atom reacts slowly with nitrous oxide. Irradiating an aqueous solution, saturated with nitrous oxide, is a convenient way of converting the hydrated electrons to OH radicals.

$e^-_{aq} + N_2O \rightarrow N_2 + O^-$

$N_2 + O^- + H_2O \rightarrow {}^{\bullet}OH + OH^-$

Argon and hydrogen are used to displace dissolved air from solutions. Hydrogen will react with hydroxyl radicals forming hydrogen atoms. Argon is an inert gas.

$H_2 + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}H$

1.2.5.1.9 Dependence of the primary yields on pH

Reactions occurring in water are greatly influenced by pH of the medium; many radicals act as acids or bases depending on pH. In either form, they still have an unpaired electron. Their reaction- rates with solutes can be different. At low pH, the hydrated electron is very rapidly scavenged by hydrogen ion and converted into H atom.

$e_{aq}^- + H^+ \rightarrow H^{\bullet}$

In highly acidic solutions, the hydrogen ions scavenge hydrated electrons within the spurs and tracks.

The H atom associates with a hydrogen ion forming H_2^+

$H^{\bullet} + H^+ \rightarrow H_2^+$

H_2^+ can readily accept electron to form molecular hydrogen and function as an oxidizing agent.

$Fe^{2+} + H_2^+ \rightarrow Fe^{3+} + H_2$

The OH radical is un- dissociated up to a pH of about 12. At higher pH it dissociates into H^+ and O^- (oxide ion). O^- is less reactive in hydrogen abstraction reactions with saturated compounds and addition reactions with aromatic compounds.

${}^{\bullet}OH + H_2O \rightarrow H_3O^+ + O^-$

The perhydroxyl radical HO_2 exists below about pH 4.5. It ionizes to O_2^- (superoxide anion) above this pH.

The yield of H_2O_2 does not change in lower pH but above a pH of 12, H_2O_2 dissociates into H_3O^+ and HO_2^-

$H_2O_2 + H_2O \rightarrow H_3O^+ + HO_2^-$

Overall radical and molecular product yields at low pH are rather higher than in neutral and basic solutions.

1.2.5.2 **Radiation Chemistry of aqueous solutions**

1.2.5.2.1 Fricke dosimeter

Radiation induced oxidation of ferrous ions to ferric ions in acid medium is one of the most thoroughly studied reactions in radiation chemistry. It is widely used as a chemical dosimetric system known as Fricke dosimeter (Fricke, Hart and Smith 1938). Ferrous- Ferric system or the Fricke dosimetric system consists of a dilute solution of ferrous ions and sodium chloride in dilute sulphuric acid in water saturated with air. The radiation induced mechanism of the oxidation of ferrous to ferric ions happens as follows.

Since the concentrations of ferrous ions and sodium chloride are low, the indirect action of radiation with water will take place prominently. OH, H, e_{aq}^-, H_2 and H_2O_2 will be produced. All e_{aq}^- will get converted into H radical because of the presence of sulphuric acid.

$e_{aq}^- + H^+ \rightarrow H^\bullet$ this is a very fast reaction.

H_2 being inert does not interfere with the chemical reactions.

Each OH radical oxidise one ferrous ion.

$^\bullet OH + Fe^{2+} \rightarrow OH^- + Fe^{3+}$

Each molecule of H_2O_2 oxidizes two ferrous ions.

$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^\bullet OH$

$^\bullet OH + Fe^{2+} \rightarrow OH^- + Fe^{3+}$

Each H radical oxidizes three ferrous ions by sequential reactions involving $HO_2^\bullet$, H_2O_2 and $^\bullet OH$ respectively.

$H^\bullet + O_2 \rightarrow HO_2^\bullet$

$HO_2^\bullet + Fe^{2+} + H^+ \rightarrow Fe^{3+} + H_2O_2$

$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^\bullet OH$

${}^\bullet OH + Fe^{2+} \rightarrow OH^- + Fe^{3+}$

the radiolytic yield of ferric ions is given by

$G(Fe^{3+}) = G({}^\bullet OH) + 2\,G(H_2O_2) + 3\,G(H^\bullet)$

The established radiation chemical yield of ferric ions is 1.61 $\mu molJ^{-1}$ for Co-60 gamma radiation.

Oxygen is consumed during the course of radiolytic reactions. But the yield of ferric ions is not affected by the change in concentration of oxygen as long as even a very small concentration of oxygen is available for reactions. When oxygen is fully exhausted or totally absent, the radiation mechanism is affected and the yield falls. H will directly oxidize one ferrous to ferric ion.

$H^\bullet + Fe^{2+} + H^+ \rightarrow Fe^{3+} + H_2$

The oxidation of ferrous by $^\bullet OH$ and H_2O_2 does not change.

The radiolytic yield of ferric ion in the absence of oxygen is given by

$G_{Fe\,3+} \rightarrow G({}^\bullet OH) + 2\,G(H_2O_2) + G(H^\bullet)$

And the yield falls to 0.85 $\mu molJ^{-1}$

Organic impurities (RH) can increase the yield of ferric ion in aerated solutions by the seqence of reactions

$OH + RH \rightarrow R^\bullet + H_2O$

$R^\bullet + O_2 \rightarrow RO_2^\bullet$

$RO_2^{\bullet} + H^+ + Fe^{2+} \rightarrow Fe^{3+} + RO_2H$

$RO_2H + Fe^{2+} \rightarrow Fe^{3+} + RO^{\bullet} + OH^-$

$RO^{\bullet} + H^+ + Fe^{2+} \rightarrow Fe^{3+} + ROH$

Each OH radical brings about oxidation of three ferrous ions instead of one ferrous ion when an organic impurity like RH is present. Depending upon the nature of the organic compound present, oxidation of ferrous becomes a chain reaction leading to uncontrollable and spuriously high yields of ferric ions. The ferrous to ferric ion conversion cannot be then used as a reliable dosimetric system.

In order to overcome the influnce of organic impurities and undisirable chemical changes in the dosimetric solution, use of very pure triple distilled water or addition of a small amount of sodium chloride is recommended and special care during preparation and handling of the solution should be taken.

Fricke dosimeters are currently used for dosimetry exercises and calibration of radiation sources. The dosimeters are easy to prepare and most widely used.

1.2.5.2.2 FBX Dosimeter

This low-level dosimeter developed in BARC consists of Ferrous ammonium sulphate, Benzoic acid Xylenol Orange (FBX) in dilute solution of sulphuric acid in aerated water. As in the Fricke system, the reaction involved is the radiation-induced oxidation of ferrous ions to ferric ions by the primary species produced on radiolysis of acidified water, viz. OH, H, and H_2O_2. OH and H radicals initiate a chain reaction with benzoic acid (BA) whereby a large number of ferrous ions is oxidized to ferric ions. Xylenol orange (XO) is a dye, which forms a coloured complex with ferric ions. It does not complex with ferrous ions. The ferric-xylenol orange complex has a higher absorbance compared to ferric ions. This helps in measuring lower concentrations of ferric ions using a spectrophotometer. Presence of BA and XO in aqueous and acidified ferrous solution sensitizes enables this dosimeter measure doses in the therapy level.

The highly reactive $^\bullet$OH and $^\bullet$H react with all the three dissolved solutes viz. BA, XO and ferrous ions. Taking into consideration the reactivity of these radicals with these solutes, their concentrations are optimized in such a way that OH and H react preferentially with benzoic acid and form adducts known as cyclohexadienyl radicals (reactions 2&3). These adducts react with oxygen (from the dissolved air in the solution) and form peroxy cyclohexadienyl radicals (reactions 4&5). The peroxy radicals initiate a chain reaction by which a large number of ferrous ions are oxidized to ferric ions. Thus, benzoic acid sensitizes the radiolytic oxidation of ferrous to ferric ions or the radiolytic yield of ferric ion increases in presence of benzoic acid.

The initial reactions in FBX can be written as

H_2O ^^^->$^\bullet$OH, $^\bullet$H, H_2O_2 ----------(1)

$C_6H_5COOH + {}^\bullet OH \rightarrow {}^\bullet C_6H_5(OH)\ COOH$ ----------(2)

$C_6H_5COOH + {}^\bullet H \rightarrow {}^\bullet C_6H_5(H)\ COOH)$ ----------(3)

$C_6H_5^\bullet\ (OH)\ COOH + O_2 \rightarrow {}^\bullet C_6H_5(OH)\ O_2COOH$ ----------(4)

$C_6H_5^\bullet\ (H)\ COOH + O_2 \rightarrow {}^\bullet C_6H_5(H)O_2\ COOH$ ---------(5)

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^-$ ---------(6)

A small concentration of XO participates in reactions with $^\bullet$H and $^\bullet$OH radicals, controls the chain oxidation and gets decolorized. But, majority of XO forms complexes with the ferric ions giving rise to visibly coloured complexes. The concentration of ferric-XO complex can be measured in the visible region with a spectrophotometer. The molar absorption coefficient of the coloured complex at the wavelength of maximum absorption in the visible region is about nine times higher as compared to the value of ferric ions in the UV region. Thus, use of XO sensitizes the ferric ion concentration measurement. A combination of benzoic acid and

XO in aerated aqueous acidified solution are used as radiolytic and analytical sensitizers for oxidation of ferrous and measurement of ferric ions, respectively. The sensitization helps to measure lower absorbed doses compared to the Fricke dosimeter (Hart 1952). “Chemical reactions of organic compounds with X-ray activated water.” *J. Chem. Phys* 6 (1938): 229-240.)

Oxygen is very important for the benzoic acid sensitized ferrous oxidation. There is no chain reaction in the absence of oxygen. The radiolytic yield of the ferric-XO complex depends on the amount of dissolved oxygen present. The initial $G_{\text{Ferric-XO}}$ in aerated solution is 55.9 $x10^{-7}$ $molJ^{-1}$.

Oxidation of ferrous to ferric ions and formation of ferric-XO complex is predominant initially and the amount of ferric-XO complex formed is linearly proportional to dose or energy absorbed. When the ferric-XO complex concentration builds up, it also participates in the reactions and undergoes reduction. Oxidation of ferrous to ferric competes with reduction of ferric complex. The amount of ferric-XO complex versus absorbed energy becomes non-linear because of the competitive reactions. Since FBX dosimeter consists of three solutes participating simultaneously in reactions with the radicals at different rates and amounts, the radiation chemical reactions are very complex. All the reaction steps by H, OH and H_2O_2 leading to ferric-XO complex are not fully established. Observations from many experiments show that the number of ferrous ions oxidized initially by each H, OH and H_2O_2 are 8.5, 6.6 and 7.6 respectively in aerated FBX. About 8% OH reacts with XO and the remaining with benzoic acid. The fractional values are due to this competition. There is competition between H reactions with oxygen and benzoic acid, but both leads to the production of H_2O_2, which leads to further ferrous oxidation. Even though the mechanism involving the chain reaction is complicated, it is reproducible within 0.3%. FBX system is standardized against the Fricke dosimeter and approximately 35 times more sensitive than the Fricke system and finds wide use in radiotherapy and radiation biology. FBX dosimeters are used to calibrate low dose delivery devices like blood irradiators.

It has been observed during experiments that the dissolution step of benzoic acid is time consuming and can lead to erroneous results if not done properly due to increased oxidation of ferrous.

1.2.5.2.3 Ceric–Cerous

Acidic aqueous solutions of tetravalent cerium ion salts have long been used for measuring large doses of ionizing photon radiation. Ceric sulfate hydrate [Ce $(SO4)_2 \cdot H2O$] or ceric ammonium sulfate is used at different concentrations (0.2 mol m^{-3} to 50 mol m^{-3}) to cover different portions of the dose range from 0.5 kGy to 100 kGy. The basis of the ceric sulfate dosimeter is the radiolytic reduction of ceric (Ce (IV)) ions to cerous (Ce (III)) ions in acid solution. The amount of ceric ion reduced to Ce (III) can easily be measured by ultraviolet/visible spectrophotometry.

The ceric sulfate system has demonstrated sufficient accuracy and reproducibility for reference dosimetry. However, in the preparation and analysis of the ceric sulfate dosimeter, purity of water and cleanliness of apparatus are important considerations since the reaction is affected by even trace quantities of organic impurities.

Another system, commonly referred to as the ceric–cerous dosimetry system, uses approximately equal initial concentrations of ceric and cerous ions to reduce the effects of organic impurities. The ceric–cerous dosimeters can be measured by either potentiometric or spectrophotometric methods. The measurement of the electropotential difference between irradiated and unirradiated dosimeters eliminates the step of dilution of the dosimeter solution required for spectrophotometric analysis and allows the use of ceric–cerous dosimeters for routine dosimetry.

Stability

The ceric dosimeter in sealed glass ampoules has excellent stability before and after irradiation when stored in the dark. Irradiated and unirradiated ampoules stored for more than two years have been found to have the same absorbance and radiation-response characteristics.

These dosimeters are made in India by BRIT and at present are the only indigenously manufactured dosimeter systems available commercially and supplied to radiation processing facilities at reasonable cost.

The lower range is limited to 1 kGy (sensitive to organic impurities makes it non reproducible at low doses) being the only drawback. Although many attempts were made to bring down the range, no positive results were reported.

1.2.5.2.4 Dichromate

The basis of the dichromate dosimeter is the radiolytic reduction of dichromate Cr (VI) ions to chromic Cr(III) ions in acid solution. The amount of highly colored dichromate ion reduced to Cr (III) can easily be measured by ultraviolet/visible

The Ag(II) species is capable of oxidizing chromium, but will not react with molecular hydrogen. In addition, the dose-rate dependence is suppressed because the OH radical concentration does not build up to the levels at which the dimerization reaction to form H_2O_2 becomes significant.

Dose range: 2 kGy to 55 kGy

Few dosimeter batches were prepared indigenously, however the dosimeters response was found to be inconsistent.

1.2.6 Radiation Chemistry of solids

All types of ionizing radiation produce ionization and excitation in solids as in other states of matter. The yields of ions, electrons and excited states produced by exposing an organic compound are independent of the physical state. The nature and yields of the final products are dependent on the state. A variety of effects are observed on irradiation, depending on the nature of the radiation and solid. Radiation effects are similar for the same compound in whichever form it exists. Density and temperature are two important factors affecting the reactions of the initial species. Some of the important features of radiation chemistry of solids are follows. De-excitation of excited molecules competes more efficiently with decomposition because of the closely packed nature of molecules. The dissociated fragments may promptly recombine at the site of production because of cage effect. So the radiation chemical yields are considerably lower. Smaller species like e^- or H atom migrate through the solid matrix and may get trapped. Since the distance traveled by an energetic electron depositing its energy is inversely proportional to the density of the medium, the tracts are shorter and the spur radii are smaller. There is an increased role intra - spur reactions of radicals, electrons and cations. Physical trappings of electrons prolong the life of the +ve ions and subsequent ion-molecule reactions. Trapping of charges may also reduce the energy available from neutralization processes. Since diffusion rates are slow; storage of electrons, ions and radicals (sometimes at lower temperatures) is possible. Heating or exposure to UV light can sometimes mobilize trapped species, giving rise to thermoluminescence and photoluminescence.

Solids as dosimeters

In most radiation chemical studies of solids the more penetrating low LET radiation is used. Changes produced by absorption of radiation by solids can be used to measure absorbed doses.

When amino acids are irradiated, the free radicals produced are trapped in the solid matrix. The radicals are stable at room temperature. They are estimated by ESR, lyoluminescence or spectrophotometric techniques.

1.2.6.1.1 Alanine dosimeters (EPR readout)

EPR spectroscopy of the amino acid α-alanine is used for measuring absorbed doses of ionizing radiation in the dose range from 1 Gy to 100 kGy. Alanine EPR is available in with various foreign based companies like Bruker, Germany (Figure 1.9). Electron paramagnetic resonance spectroscopy is non-destructive that is suitable for reference standard, transfer standard, and routine dosimetry.

Each Alanine dosimeter costs about 150 rupees (Film dosimter is costlier). The spectrometer can cost up to 65-70 Lakh rupees and since it is not manufactured in India we have to depend on supplier for maintenance and servicing.

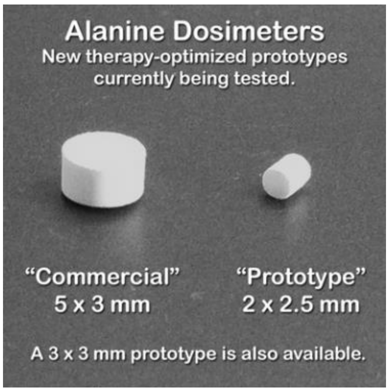


Figure 1.9: Alanine Pellet Dosimeter

1.2.6.1.2 Dyed Perpsex dosimeters

Figure 1.10: Dyed Perpsex dosimetersv (Harwell Red 4034 Dosimeters (United Kingdom))

Perspex dosimeters are made from radiation-sensitive poly-methylmethacrylate (PMMA) in the form of optically transparent pieces individually sealed in laminate sachets. They darken when irradiated, and the radiation-induced darkening, accurately measurable by means of a spectrophotometer, is a function of the radiation dose absorbed.

Harwell Red 4034 Dosimeters (United Kingdom) (Figure 1.10) are commercially available. The dosimeters have a functional dose range of 0.1 kGy to 50 kGy with good reproducibility which makes it ideal for a wide range of irradiation processes. However post-irradiation stability is limited due to humidity effects and colour reversing is observed on keeping for more than 15 days therefore cannot be used for record keeping.

1.2.6.1.3 Radiochromic film

Figure 1.11: Radiochromic film dosimeter

Figure 1.12: Radiochromic film RisoB3 dosimeter

Radiochromic films (Figure 1.11) employ use of triphenyl methane cyanide dyes like hexa (hydroxyethyl) pararosaniline cyanide in nylon or polyvinyl butyral matrix. Its advantage is that each dosimeter is uniquely numbered and bar-coded for quick scanning and absolute traceability. The dosimeter is packaged within a transparent pouch protecting the B3 film from stray UV radiation, allowing barcode scanning of the dosimeter through the sealed pouch, and providing a long shelf-life.

Specifically, B3 dosimeters (Riso, Denmark) (Figure 1.12) can be used to measure ionizing radiation doses from gamma, X-ray and electron beam sources, including low energy electron sources, with a dose range from <1.0 kGy to > 150 kGy.

The dosimeter cost is very high and the spectrophotometer and uses toxic cyanide in its manufacture process.

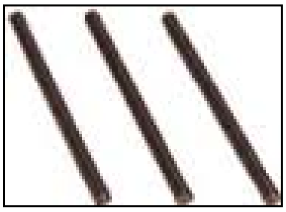


Figure 1.13: FWT-70 Opti-Chromic Dosimeters (FWT-70-40M, FWT-70-83M)

This is based on a liquid or gel core of radiochromic solution held in 2.7 mm outer diameter fluorinated-ethylene polymer tubing that is typically 5 cm long, with light transmitting seals at both ends. The dosimeters are analyzed for dosimetry by a dedicated spectrophotometer, using a narrow spectral band of light corresponding to the region of the optical absorption band peak or to wavelengths on the high-wavelength shoulder of the optical absorption band. Absorbed doses in the range 1 Gy to 10 kGy can be measured using this method, with a reproducibility of 10 % (2σ).

FWT-70 series of Opti-Chromic Dosimeters (Figure 1.13) are designed for low level radiation processing. They are small optical waveguides that gradually changes from clear to deep blue in relation to absorbed dose. The sensitivity ranges from 10 Gy to 20 kGy depending on the model.

The dye is derived from the family of aminotriphenyl-methane. These dyes can be made radiochromic that change from colorless to a deeply colored state as a function of absorbed dose. The FWT-70 series of dosimeters use hexa (hydroxyethyl) aminotriphenylacetonitrile (HHEVC) dye inside an optical waveguide. Readout of the dosimeters is by photometric means using dual wavelength photometry.

Along with the high cost this dosimeter can be specifically measured by waveguide spectrophotometer that is supplied by the manufacturer. The maintenance and cost add to the total cost of dosimetry.

1.2.6.1.4 Cellulose triacetate films

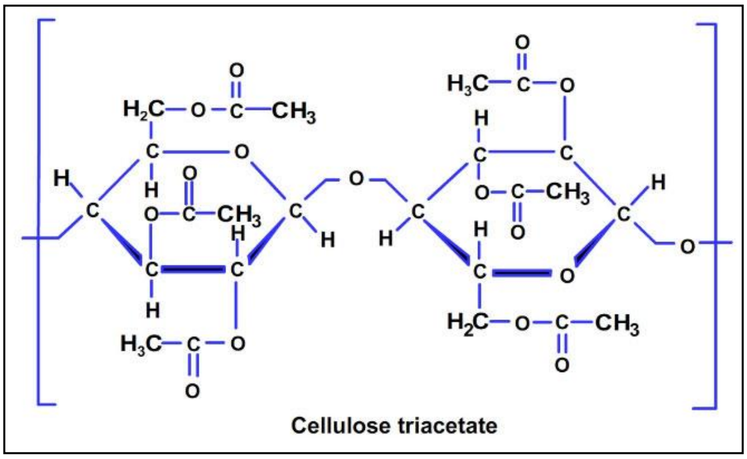


Figure 1.14: Chemical structure of Cellulose triacetate

Figure 1.15: Cellulose triacetate dosimeter film

Absorbed dose is evaluated from the measured value of the increment of the optical density at the wavelength of 280nm induced by radiation. The optical density can be measured with ordinary U-V spectrophotometers with usable dose range 5kGy – 300kGy. The films are composed of cellulose triacetate (Figure 1.14) and triphenyl phosphate. The film has a thickness of 125μm (~15mg/cm^2).

The films are imported from Japanese based company Fujifilm (Figure 1.15), and at present the supply to Indian market is limited due to restrictions at their end.

1.2.6.1.5 Lithium Fluoride Photo luminescent System (Sunna Film Dosimeters)

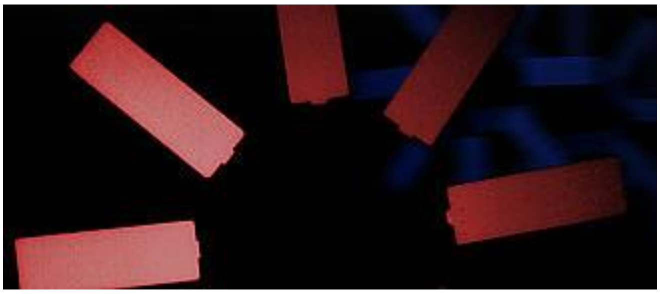


Figure 1.16: Sunna Film Dosimeters

The Sunna Dosimeter (trademark) (Figure 1.16) is a small, plastic wafer that is being marketed to accompany food products during irradiation (cold pasteurization). The dosimeter ensures that products receive doses within regulatory requirements.

The radiation-induced color centers in pure LiF, especially the M-center, are also photo luminescent, and emit characteristic green and red light when excited by wavelengths in the blue. The intensity of the light emitted provides the dose value that the food received, with a high degree of accuracy. This optically stimulated luminescence effect has recently been applied to a commercially available high-dose dosimeter, consisting of microcrystalline pure LiF suspended in a polymeric film matrix. The dosimeter is a flexible, white, opalescent plastic film with dimensions 10 mm × 30 mm × 0.5 mm. It is useful for dosimetry in the absorbed-dose range from 0.3 kGy to 250 kGy when measuring in the green and from 0.05 kGy to 200 kGy in the red, with an estimated uncertainty of 6 % (2σ). The dosimeters are costly and availability is limited in Indian market.

1.2.6.1.6 Polydiacetylene-based Systems

With the polydiacetylene dosimetry films, e.g., GafChromic HD-810 (Figure 1.17, Figure 1.18) or MD-55, the radiation-induced colored forms are built up through solid-state polymerization of the diacetylene monomers by progressive 1,4-trans additions.

Polyconjugated linear molecules are linked, leading to partial polymerization (oligomerization). In this system, the chromophores are ladder-like polymer chains occurring as a series of polyconjugated double bonds along the carbon backbones. The working dose range is suitable for low dose applications

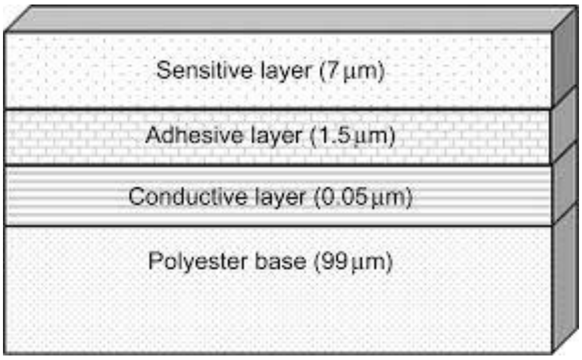


Figure 1.17: Layers in Gafchromic dosimeter

Figure 1.18: Gafchromic film

These dosimeters are used in low dose application especially in medical dosimetry. They are extremely reproducible however the range restricts its widespread use in radiation processing.

1.2.6.1.7 Radiation Indicators

Radiation Indicators are ideal for maintaining inventory and quality control. By labeling products with radiation indicators you can have a visual indicator of whether or not a product has been exposed to ionizing radiation, aiding in the segregation and of product for inventory control. This provides an additional quality control check but is not a substitute for proper dosimetry. It can also be used during an irradiation process to provide visual identification of single and double-sided processed products.

Polymeric films like polymethyl methacrylate (PMMA), polyvinyl chloride (PVC) dyed PMMA are proposed for high level dosimetry. Interaction of radiation results in changes that are used for dose measurements. PMMA gets coloured when exposed to radiation. The formation of transient species (trapped electrons and/or free radicals) produced in good yield, are responsible for the colour. PVC also becomes highly coloured on irradiation. Trapped electrons and/or free radicals and formation of conjugated double bonds in the polymer are the reasons for the colour formation. On irradiation HCl is lost from the PVC molecule $[CH_2\text{-}CHCl\text{-} CH_2\text{-}CHCl]_n$. The double bonds formed labilize the atoms in the α position, so that further loss of HCl molecules will tend to occur in positions adjacent to the first in the overall reaction. The formation of conjugated double bonds shows up as characteristic ultraviolet absorption bands. Acid produced from PVC on irradiation can change the colour of a pH indicator (dye) incorporated in it. The dose is found out by visual optical colour comparison of irradiated and unirradiated specimens. They are used as go-no-go indicators such as paints labels etc.

Figure 1.19: GEX radiation Indicators (high dose range)

Figure 1.20: Blood Irradiation Indicators (low dose range)

They are for use in gamma, electron beam and X-ray sterilization applications. They turn from an un-irradiated yellow-orange color to red at 3.0 kGy, and on to a red-purple at 10 kGy and above (Figure 1.19). More sensitive indicators are used for low dose applications such as blood irradiation indicators (Figure 1.20).

Limitations

Indicators may not adhere well to certain polymers such as polypropylene and certain rough cardboards. Infrequent false positive or false negative results may occur. Generally any small failure of a few dots cannot be investigated for cause due to the sample size. Exposure to direct sunlight or intense UV light can give false positive results.

Polyvinyl butyral coating with an ethanol - based dye is the basic composition. The actual reagents used are closely guarded and patented.

Indigenously manufactured radiation indicators are observed to be less stable. Their sensitiveness to environmental condition makes them a lesser chosen alternative.

1.2.7 **Radiation Chemistry of gases**

Ions, excited molecules and radicals are formed initially on irradiation of gases. Since gaseous molecules are not closely packed, these transient species are not confined to particle tracks and spurs. Track and spur effects seen with condensed phases are therefore not important in gases and LET effects are not observed. They diffuse freely, rapidly and get uniformly distributed throughout the medium and reactions between transients or transient and gaseous molecule are less likely to happen. The transient species have longer lifetimes and they lose energy more slowly as the collision rate is lower. The radiation chemistry of gases is more complex with numerous excited state reactions and ion-molecule reactions. Solvation and stabilization of energy-rich transients by collision are not significant. The walls of the gas container interfere and many energy-rich reaction products lose energy by collision with the walls.

Oxygen is converted into ozone on exposure to ionizing radiation or an electric discharge. The following mechanism is suggested for the formation of ozone in irradiated oxygen.

Ozone is produced around high intensity irradiators by these mechanisms and poses a health hazard. Suitable ventilation and a number of air changes are recommended in these installations. Ozone formation is important for seal packed dosimeters like the film dosimeters. Ozone reacts with many organic reagents and thus can interfere with dosimeter response.

1.3 Objectives of the Thesis and Layout of the report

Keeping in view the objectives of our studies, the thesis has been arranged in five different chapters depending on the applications. Chapter 1 describes the subject of the thesis in detail with reference to the systems studied and this chapter is named as general introduction. Chapter 2 details about the experimental and instrumental part. Other analytical techniques, material purification etc. have also been covered in this chapter.

Chapter 3 describes the development of Ferrous Sorbitol Xylenol Orange dosimeter. It is improved version of its predecessor FBX. With sorbitol as readily water soluble sensitizer as replacement to benzoic acid it can measure low doses with good reproducibility. Sorbitol is used as a radiolytic sensitizer in Ferrous Xylenol Orange based system for measuring low doses with high reproducibility. Being a liquid dosimeter it can be used for dosimetry of complex shapes and geometries. Using FSX, low dose irradiation units such as blood irradiators and gamma chambers can be standardized. Being highly reproducible it can be used for calibration of low activity sources, using Fricke dosimeter used as reference.

Chapter 4 describes a new technique for radiation chemical synthesis erythrosine from fluorescein. Further, use of this reaction for development of radiation processing indicator is discussed. Borax and molybdate were found to increase the reaction rate and thus used as catalysts. A radiochromic dosimeter with linear response and good reproducibility is developed as further extension of the radiation indicator. Both the systems display a contrasting colour change that is specific to radiation dose.

Chapter 5 is about conversion of radiation indicator to radiation indicator gel by establishing its performance. The radiation gel developed can be used for record keeping and is ready for application without any further modifications. Along with this a radiation indicator film was developed that can be used as go-no go indicator for radiation processing applications.

The last chapter summarizes all the systems studied and developed, finally concluding the thesis.

Chapter 2 Experimental Techniques

A brief overview of the different experimental techniques used has been illustrated in this chapter. Overview of irradiators with the working principle of Gamma Chambers (GC-900 and GC -1200) used as an irradiation source, radiation processing facilities, and electron accelerator has been explained. Role of chemical dosimetry in radiation processing with use of calibration procedures for standardizing is explained in detail. Role of UV-visible spectrophotometer and EPR Spectroscopy used for calibration of dosimeters is also highlighted

2.1 Category of Gamma Irradiators

The irradiators are categorized in terms of the design of the irradiator with respect to configuration of the product irradiation position, accessibility and shielding of radioactive source.

Category-I: Self-contained, Dry source storage

An irradiator in which the sealed source is completely contained in a dry container constructed of solid materials, the source is shielded at all times, and human access to the sealed source and the volume undergoing irradiation is not physically possible in its designed configuration.

Category-II: Panoramic, Dry source storage

A controlled human access irradiator in which the sealed source is contained in a dry container constructed of solid materials, the source is fully shielded when not in use; the sealed source is exposed within a radiation volume that is maintained inaccessible during use by an entry control system.

Category-III: Self-contained, Wet source storage

An irradiator in which the sealed source is contained in a storage pool (usually containing water), the source is shielded at all times, and human access to the sealed source and the volume undergoing irradiation is physically restricted in its designed configuration and proper mode of use.

Category-IV: Panoramic, Wet source storage

A controlled human access irradiator in which the sealed source is contained in a storage pool (usually containing water), the sealed source is fully shielded when not in use; the sealed source is exposed within a radiation volume that is maintained inaccessible during use by an entry control system.

2.2 Radiation source used for irradiation

The first group consists of the classical radiation sources, radium and radon, and artificial isotopes such as ^{60}Co, ^{137}Cs, and ^{90}Sr-^{90}Y. The second group consists of X-ray generators, electron accelerators, other particle accelerators. Nuclear reactors have also been used as radiation sources for neutron beams and indirectly by using loops of liquid metal or alloys.

Of the few isotopes separated initially ^{137}Cs emerged as a promising star. It emitted gamma ray photons with 0.66 MeV energy and had a relatively long half-life of thirty years. However owing to the inconvenient and expensive extracting procedure its supply and demand was unbalanced.

At this time another extremely useful radioisotope ^{60}Co was discovered not as a fission product, as a by- product. ^{60}Co was produced by neutron activation of ^{59}Co in nuclear reactors.^{59}Co absorbs neutron to become radioactive ^{60}Co.It has half-life of 5.27 years. Cobalt is a water insoluble metal with high melting point and is thus well suited radiation source for radiation processing applications. It emits two gamma rays of energy 1.17 MeV and 1.33 MeV with an average energy 1.25 MeV.

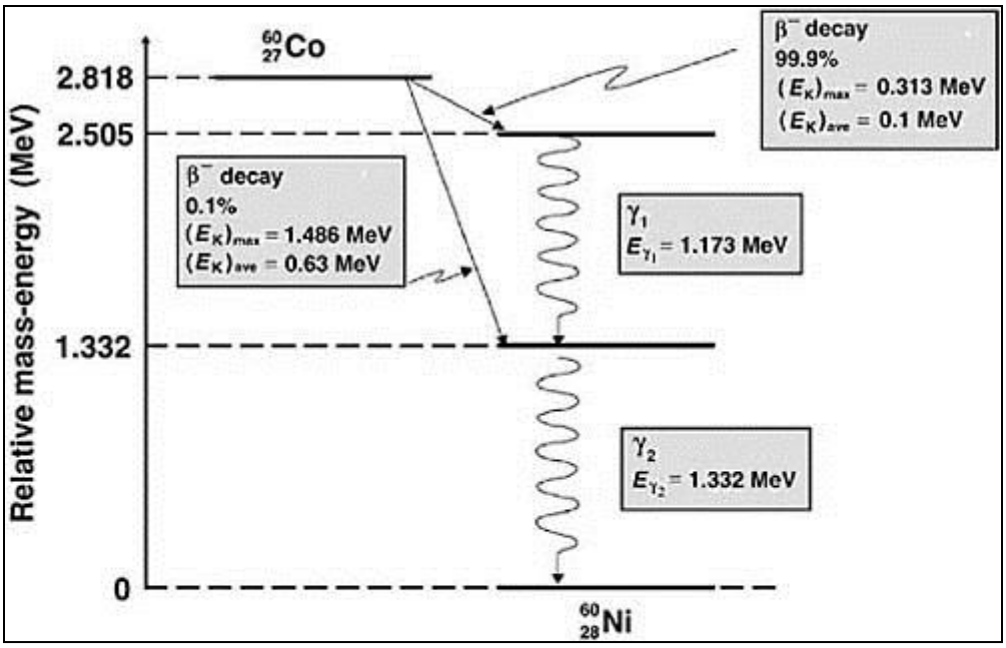


Figure 2.1: Decay Scheme of ^{60}Co

2.3 Gamma Irradiation Chamber (Gamma Chamber)

Gamma Chamber is a type of Self-Contained Dry Source Storage Gamma Irradiator. In this irradiator sealed gamma sources are completely contained in a dry container constructed of solid materials. The radiation sources are shielded at all times, and human access to the sealed sources and the volume undergoing irradiation is not normally possible in its design configuration

Radiation field is provided by a set of stationary cobalt-60 sources (Figure 2.2) placed in a cylindrical cage. The sources are doubly encapsulated in corrosion resistant stainless steel pencils and are tested in accordance with international standards. Two access holes of 8 mm diameter are provided in the vertical drawer for introduction of service sleeves for gases, thermocouple, etc. A mechanism for rotating/stirring samples during irradiation is also incorporated. The lead shield provided around the source is adequate to keep the external radiation field well within permissible limits. A typical Gamma Chamber unit (Figure 2.3) can be installed in a room measuring 3 metres X 3 metres X 3 metres.

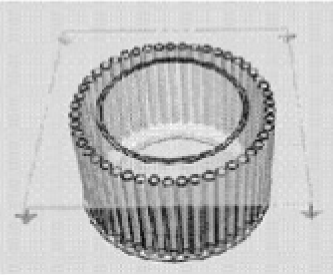


Figure 2.2: Gamma Cell 220 Source Pencil Arrangement

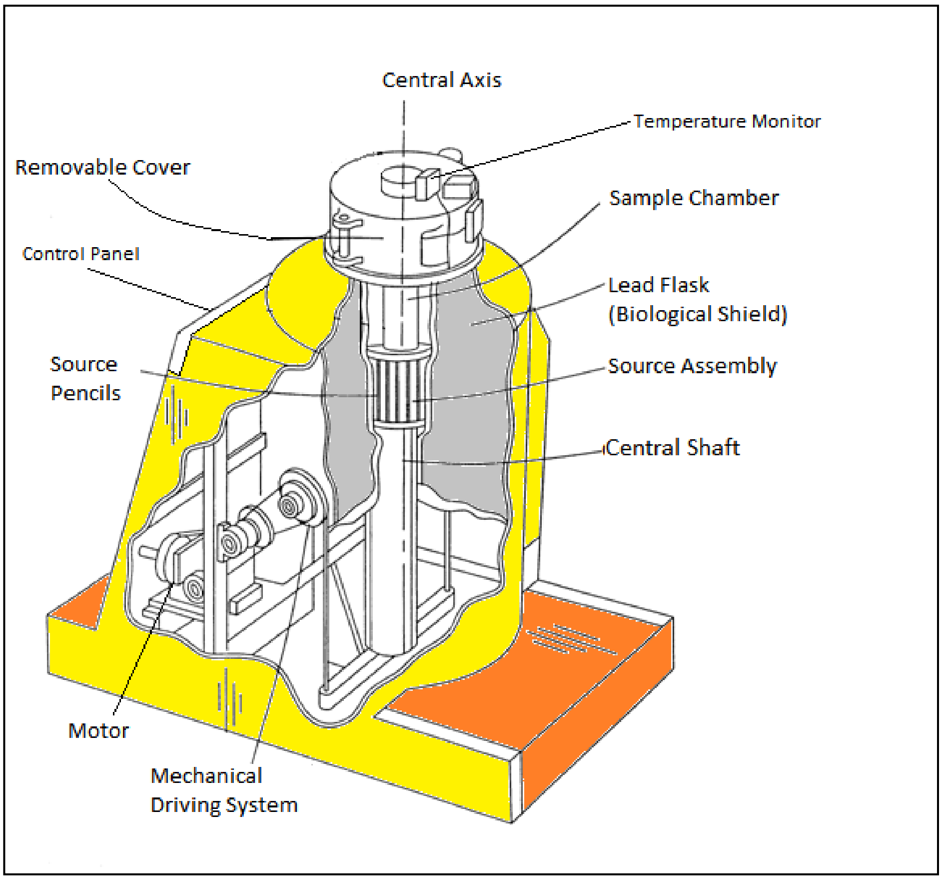


Figure 2.3: Typical Interior View of Gamma Cell

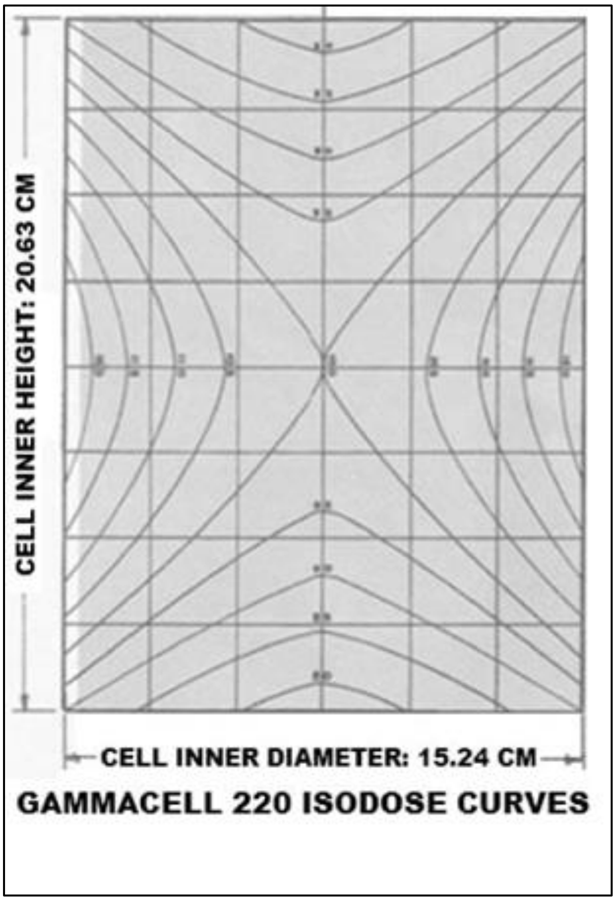


Figure 2.4: Gamma Cell 220; Isodose curves

Figure 2.4 shows typical isodose curves in Gamma Cell 220. No additional shielding is required for its installation and use. Built-in timer provides accurate control of irradiation time from 6 seconds onwards. The unit can also be operated manually. Solid state programmable controls have been provided. In the event of power failure battery backup displays the programs. It is possible to irradiate samples at low or high temperature by circulating liquid nitrogen or hot air. These can be introduced through the service sleeves provided in the vertical drawer. The irradiation temperature is sensed by a thermocouple and displayed on the panel. An additional table top control panel is provided for remote operation in addition to the normal one provided on the unit. Stationary source pencils, symmetrically placed in a cylindrical cage ensure good uniformity of radiation field in the sample chamber. In addition a mechanism is also provided for rotating/stirring samples during irradiation.

Sample chamber extends to a convenient height for easy loading and unloading of samples. The design of Gamma Chambers conforms to American National Standards. Figure 2.5 shows the typical Gamma Chamber (BRIT, India manufactured) internal view. Table 2.1 presents specification of GC-900 and GC-1200 units used extensively for irradiations during study.

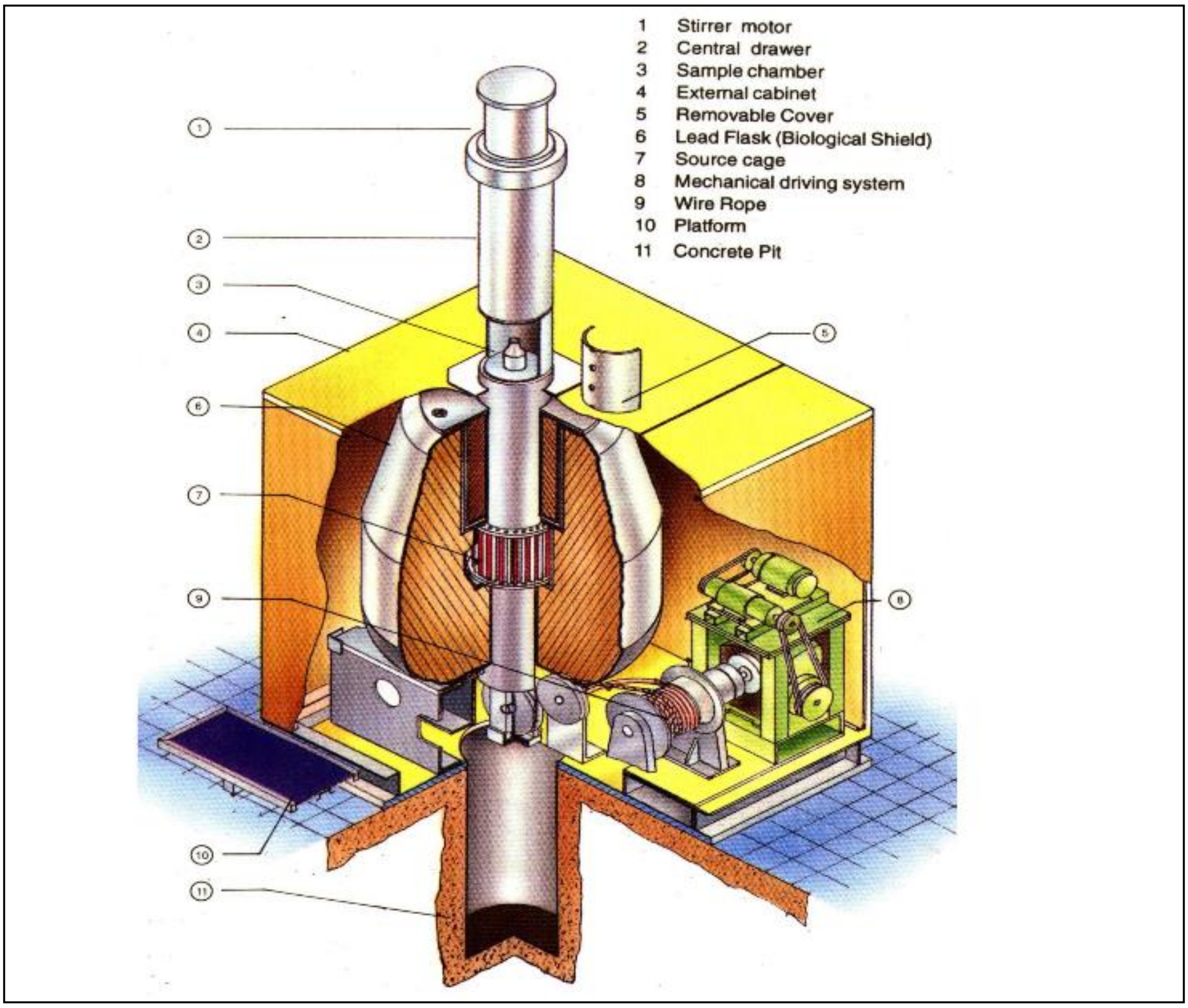


Figure 2.5: Gamma Chamber Typical Internal View(Made in Bharat by BRIT)

Table 2.1: Specification of GC-900 and GC-1200 units

Parameter	**GC-900 (Co-60)**	**GC-1200 (Co-60)**
Product launched	1970	2004
Max. Source Capacity	92 TBq, 2500 Ci	185 TBq, 5000 Ci
AERB, India Certification	Type B(M) (SS-6,1985)	Type B(U) (TSR- 1,2000)
Max. Dose rate	5 kGy/hr (82 Gy/min)	9 kGy/hr (160 Gy/min)
Sample Chamber Dimensions	100 mm Ø x 140 mm ht	106 mm dia x 140 mm ht
Irradiation volume	1.0 Ltr	1.2 Ltrs
Sample rotation system	No Provision	60 rpm
Timer range	6 sec. to 6 hrs	6 sec. onwards
Size of the Unit	80cm X 90 cm x 160 cm (ht)	110 cm x 105 cm x 158 cm
Weight of the Unit	3.0 tons	3.1 tones
Power requirement	AC single phase 220/230 V, 5A	AC single phase 220/230 V, 5A
Room size for installation	3m x 3m x 3m(h)	3m x 3m x 3m(h)
Cost of the Unit	Rs. 5 Lakhs	Rs. 18 lakhs
No. of units in use in India	63 units	1 unit
No. of units in use abroad	10 units	--

N.B.: GC 900 is older version and presently only source replenishment is being carried out

2.4 Radiation Processing Facility (RPF)

An RPF is a facility containing radiation source and associated systems used for delivering prescribed dose to a specified target in a preset time. Radiation processing technology employing gamma ray sources is used on a commercial scale for sterilization of medical products, processing of food and allied products, and vulcanization of rubber. This technology involves the use of high intensity gamma ray emitting radioisotopes such as Cobalt-60 to deliver a predetermined dose to a specific product under process conditions with access control systems for the radiation processing cell (General Aspects of Dosimetry for Radiation Processing 2008). There are a number of Gamma Radiation Processing Facilities (GRAPFs) for processing of food and allied products for various purposes such as inhibition of sprouting, insect disinfestations, delaying ripening of fruits and microbial decontamination in India with their number increasing at a steady rate. The deployment of the intense gamma ray sources in such GRAPFs poses radiation hazard for the plant personnel, public and environment in the event of any malfunction or failure of the safety systems. Atomic Energy Regulatory Board, Department of Atomic Energy exercises stringent regulatory control during design, construction and operation of such GRAPFs.

Industrial gamma radiation processing facilities have been commissioned in different parts of the country which are of different types and categories. These facilities have single or multiple shelved carriers, depending on product overlap or source overlap designs, to accommodate product boxes for radiation processing (Figure 2.6, Figure 2.7, and Figure 2.8). Plant commissioning/re-commissioning dosimetry of all these facilities is carried out to determine absorbed dose profile in food and allied products and setting of operational parameters. It involves procedures such as ensuring proper alignment of source frame to product load in carrier, carrying out dose mapping and setting irradiation time for an intended dose to be delivered to the product (ASTM-51702 2004), (The Atomic Energy (Radiation

Processing of Food and Allied Products) Rules 2012), (ISO 11137-1:2006 2006), (TRS No. 409 2002).

Standard formats for reporting the dosimetry results for obtaining the requisite license from the (Atomic Energy (Control of irradtion of food) Rules, 1996). (The Atomic Energy (Radiation Processing of Food and Allied Products) Rules 2012).

Purpose

The purpose of dosimetry is to characterize the distribution, magnitude, and reproducibility of absorbed dose in a homogeneous material for a typical range of densities and to relate these parameters with operating conditions ensuring optimum utilization of the loaded gamma ray source.

The commissioning/re-commissioning dosimetry is to be carried out after:

- Initial loading of Cobalt-60 source
    - Replenishment of Cobalt-60 source
    - Change in the source configuration
    - Change in the dimensions of irradiation cell
- Change in carrier’s path inside the irradiation cell around the source frame
- Change in the design of tote/product box/carrier.

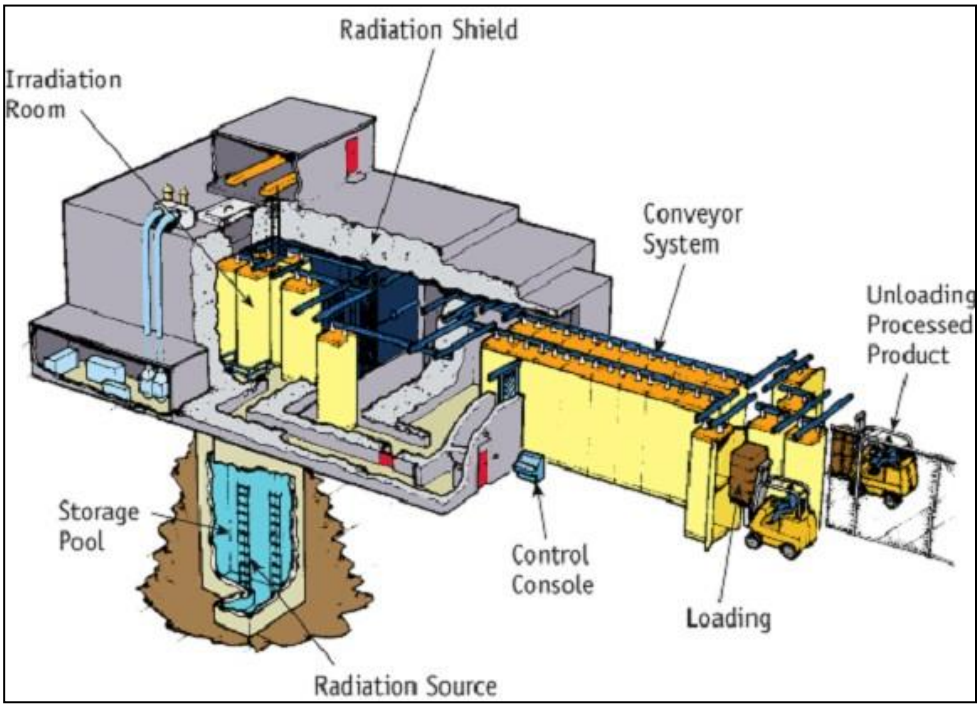


Figure 2.6: Gamma Radiation Processing Facility (GRAPF)

A radiation processing facility containing radioactive sources emitting gamma radiation and associated systems used for delivering prescribed dose to a specified target in a preset time.

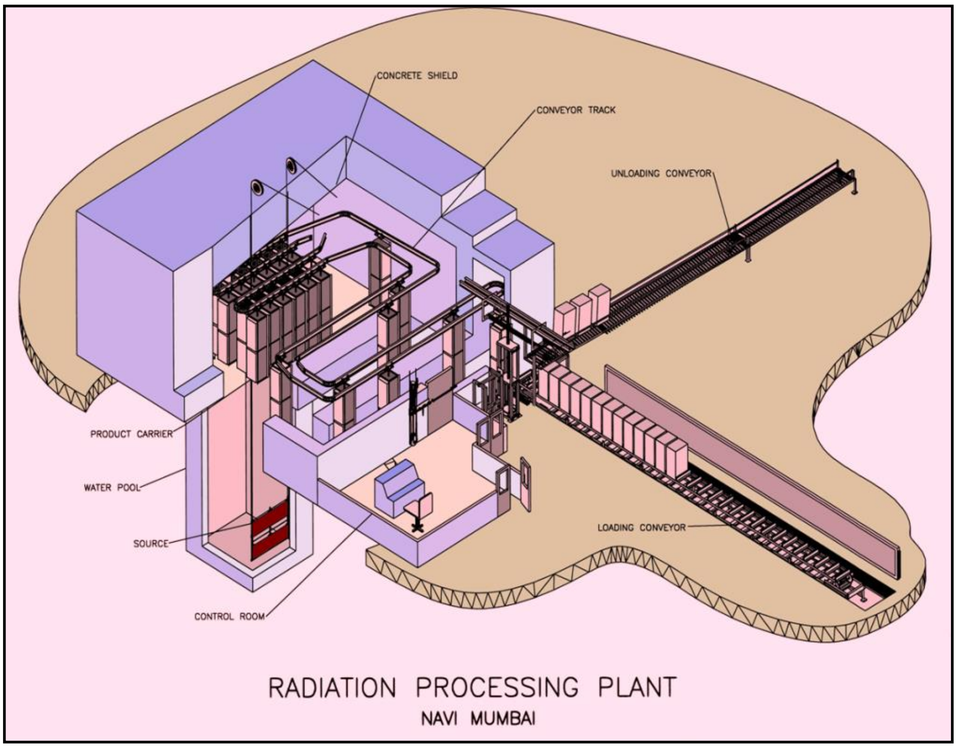


Figure 2.7: Typical Radiation Processing Facility showing Product Movement

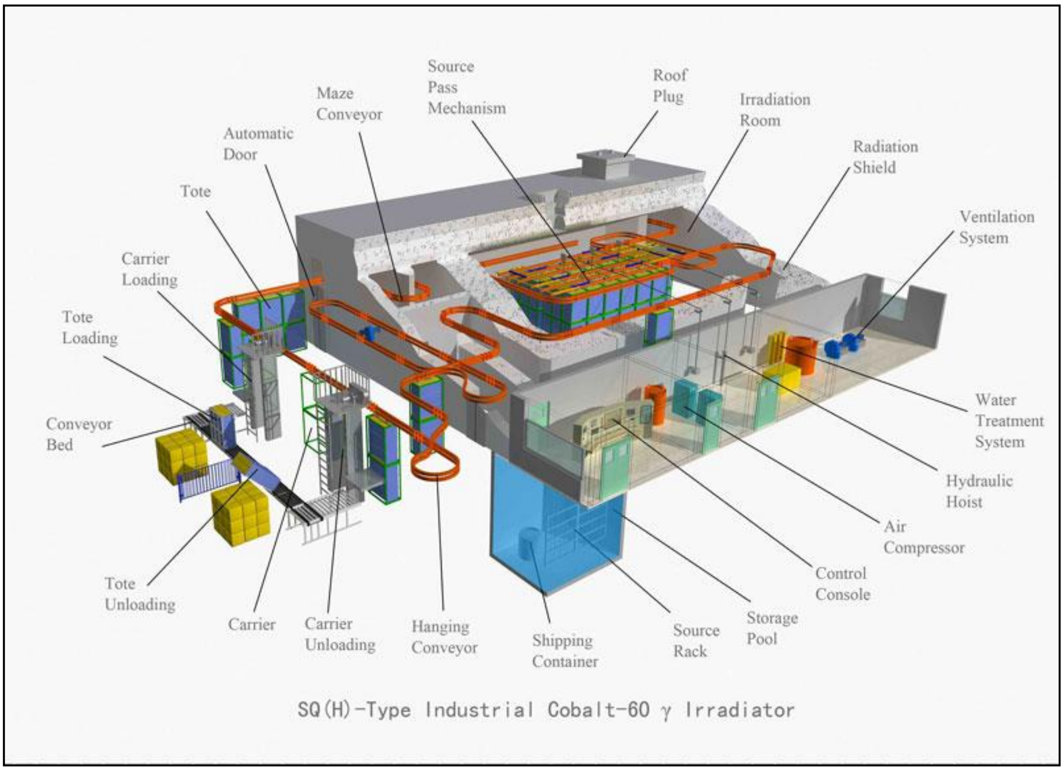


Figure 2.8: New Design of Radiation Processing Facility

2.5 Electron beam accelerators for radiation processing

At present many electron beam facilities have been installed in India for the purpose of radiation processing. Electron beam accelerators are used for radiation processing typically for processes which require high dose rates and also for surface treatments. Electron accelerators are also widely used in medical applications for radiation treatment.

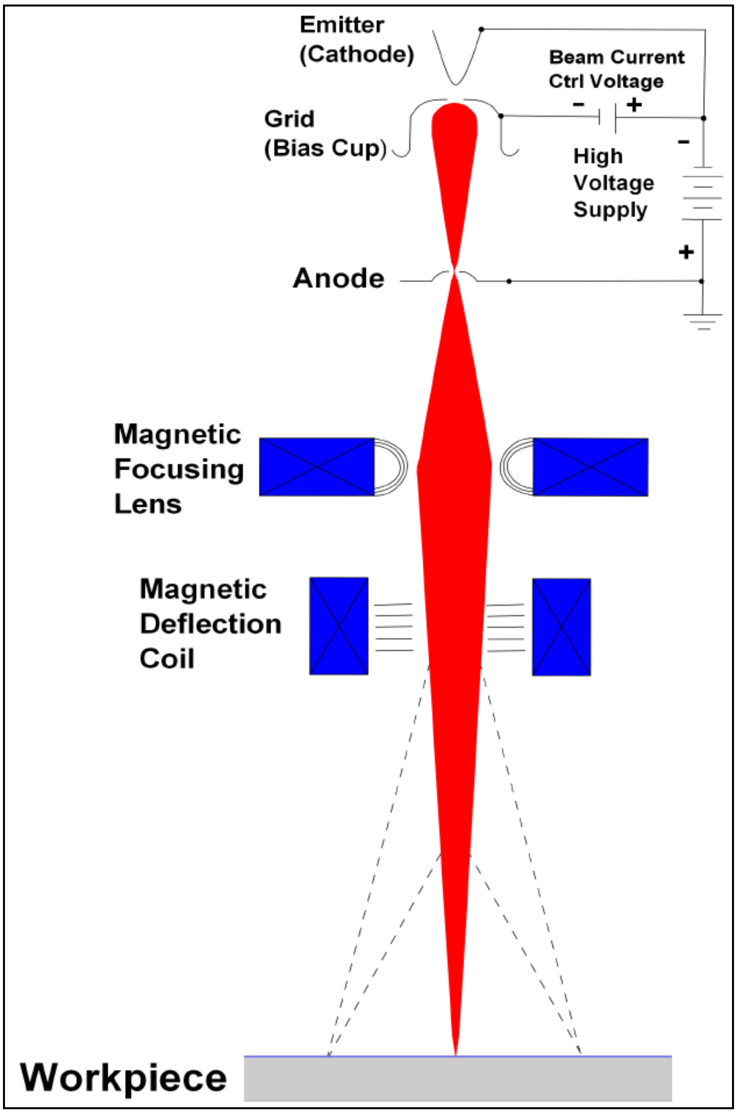


Figure 2.9: Schematic showing basic components of electron beam materials processing

Electron beam processing involves high energy electrons to treat an object for a variety of purposes. Possible uses for electron irradiation include sterilization and to cross-link polymers. Electron energies typically vary between keV and MeV range. The two basic components of an electron beam accelerator are; electron gun (consisting of a cathode, grid, and anode) that is used to generate and accelerate the primary beam and an anode with high voltage power supply for acceleration of the electron to desired energy level. The energized electron beam then passes through magnetic lens and deflector before emerging through an exit hole to the substance to be irradiated. Electron beam processing is used in industry primarily for three product modifications: Crosslinking of polymer-based products to improve mechanical, thermal, chemical and other properties, Material degradation often used in the recycling of materials, and Sterilization of medical and pharmaceutical goods (R. B. Miller 2005).

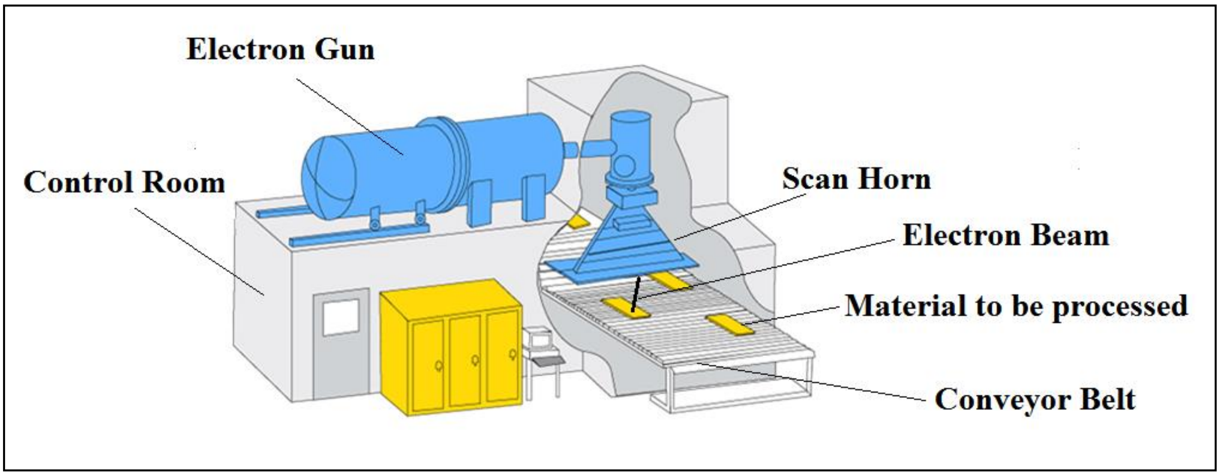


Figure 2.10: View of Electron Beam Accelerator Processing Goods

Proper dosimetry is essential to accomplish desired results using radiation processing. Several dosimetry systems are available some of which are listed in Table 2.2

2.6 X-rays generated from electron beam accelerators

In addition to this, electron beam accelerators are used to generate X-rays for applications in radiation processing of food and allied products. The energy limit was recently changed from 5 MV to 7.5 MV and internationally accepted.

2.7 Dosimetry Systems

Table 2.2: Dosimetry Systems for Radiation Processing Facilities

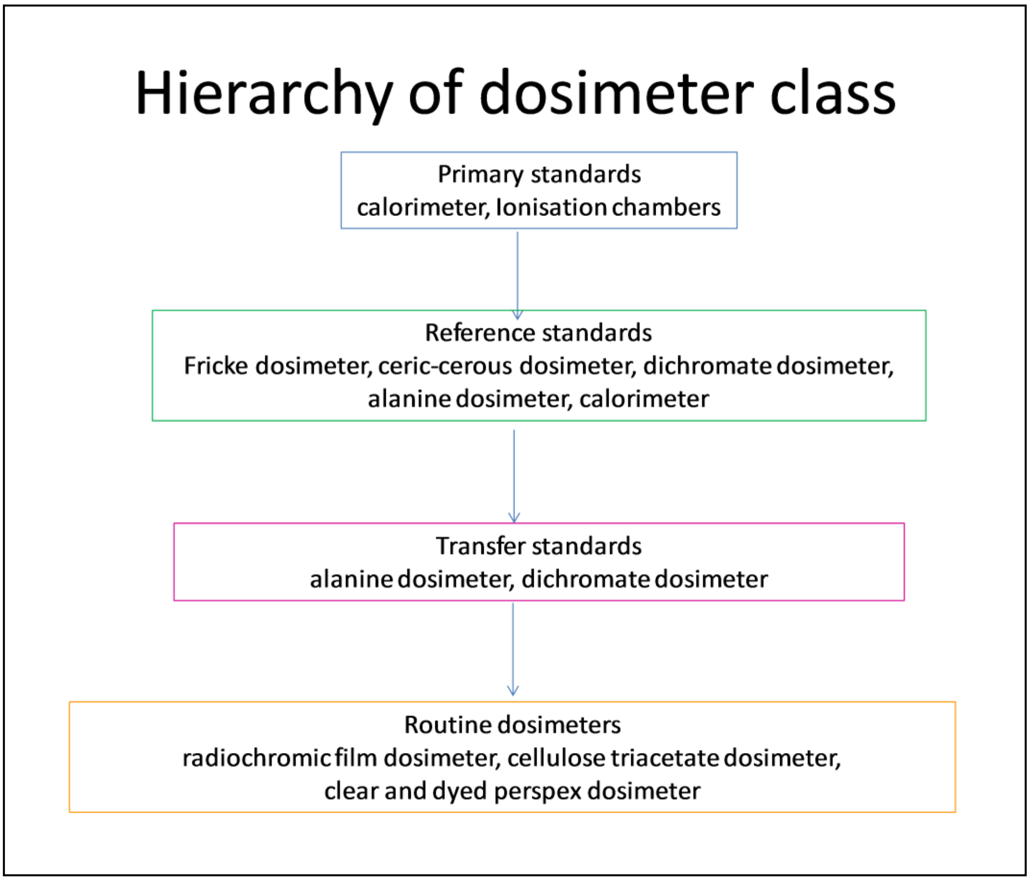
(ISO/ASTM 51261:2013(E) 2013) (ISO/ASTM51204-04 2004)

Dosimeter	Readout system	Usable absorbed dose Range in Gy	ASTM No.
Alanine	Electron Paramagnetic Resonance spectrometer	$1 - 10^5$	1607
Dyed polymethyl methacrylate	Spectrophotometer	$10^2 - 10^5$	1276
Clear polymethyl methacrylate	Spectrophotometer	$10^2 - 10^5$	1276
Cellulose tri acetate	Spectrophotometer	$10^4 - 4 \times 10^5$	1650
Lithium borate, lithium fluoride	Thermoluminescence reader	$10^{-4} - 10^3$	-
Lithium fluoride(optical grade)	Spectrophotometer	10^2-10^6	-
Radiochromic dye films solution, Optical wave guide	Spectrophotometer	1-10^5	1275 1310
Ceric Cerous sulfate solution	Spectrophotometer or potentiometer	10^3-10^5	1205
Ferrous sulfate solution	Spectrophotometer	$20 – 4 \times 10^2$	1026
Potassium/Silver dichromate	Spectrophotometer	10^3-10^5	1401
Ferrous cupric sulfate solution	Spectrophotometer	10^3-5×10^3	-
Ethanol chlorobenzene solution	Spectrophotometer, colour titration, high frequency conductivity	$10 - 2 \times 10^6$	1538
Amino acids	Lyoluminescence reader	$10 - 10^4$	-
Metal oxide semiconductor Field effect Transistor (MOSFET)	Voltmeter	1-10^2	-

(Dosimeters should be procured from a standard manufacturer conforming to the batch to batch tolerances as prescribed under the ASTM standards or as acceptable to the NSL)

2.8 Chemical dosimeters

Chemical dosimeters are dosimetry systems in which one or more chemical specie formed or destroyed or transformed by radiation is related to the dose absorbed by using suitable analytical techniques.Chemical dosimeters are preferred for dosimetry in radiation processing applications owing to many reasons. Ease of use, low cost, high reproducibility along with no special requirements for storage are some of the reasons responsible for their widespread use. Chemical dosimeters are classified depending upon the uncertainty involved with lowest uncertainty for primary standards and so on. Figure 2.11 gives the hierarchy of dosimeter class.



Hierarchy of dosimeter class

Primary standards
calorimeter, Ionisation chambers

Reference standards
Fricke dosimeter, ceric-cerous dosimeter, dichromate dosimeter, alanine dosimeter, calorimeter

Transfer standards
alanine dosimeter, dichromate dosimeter

Routine dosimeters
radiochromic film dosimeter, cellulose triacetate dosimeter, clear and dyed perspex dosimeter

Figure 2.11: Hierarchy of dosimeter class

2.9 Applications of chemical dosimetry

- Radiotherapy.
- Sterilization of medical products.
- Irradiation of blood products to decrease the occurrence of GVH (Graft Vs. Host) disease.
- Irradiation of sewage waste for decreasing the pathogen load.
- Radiation induced polymerization for producing variety of useful commodities such as polymers, composites, etc.
- Food irradiation

2.10 Characteristics of an ideal chemical dosimeter

Response of the dosimeter should be proportional to absorbed dose over a wide range, independent of dose rate, independent of the energy and LET of the radiation, independent of temperature, reproducible, stable under normal conditions such as exposure to light, pre and post irradiation stability, simple to use. Additionally, dosimeter should be easy to prepare from easily available chemicals, should not require elaborate purification of reagents, degassing and insensitive to small amounts of impurities. Response should not depend much on composition, i.e. not affected by small changes in pH, reagent concentration. In practice, no dosimeter meets all these demands with Fricke being the most well studied and widely accepted dosimeter.

2.11 Factors affecting response of Chemical Dosimeter

2.11.1 Concentration variation and effect of pH

Effect of reagents plays a vital role in chemical dosimetry. Some chemical reactions are highly dependent on the pH of the solution, although suitable buffers can be used. Orders of the reactions involved, determine the dependency of dosimeter on reactant concentration. In Fricke dosimeter, pH plays a vital role with precipitation of ferric formed at pH above 5. Hence, a comparatively high concentration of sulphuric acid is used. Along with this the acid lowers thermal oxidation of ferrous thus stabilizing the dosimeter. The effect of concentration of reagents is important as it provides a window beyond which the dosimeter fails to provide accurate results. In laboratory or commercial synthesis the quality of reagents should additionally be checked for their compatibility. It is observed that, using different brands, different origin and sometimes different batch of reagent can lead to erroneous results. To avoid this, it is always recommended to derive a new dose calibration relation before quoting any dose values. In concentration dependency study, one reagent concentration is kept constant while others are varied keeping other parameters constant. The exercise is repeated for other reagents to finalize the dosimeter composition and their concentrations.

2.11.2 Effect of dose rate

Dose rate decides number of free radicals in the irradiated medium; this is significant in liquid or aqueous systems. At high dose rates the radical- radical interactions are high due to close vicinity of these species. Radical recombinations are dominant, leading to increase in molecular products. Thus the overall reactivity due to radicals is greatly reduced. At high dose rates especially greater than 10^6 Gy/s the radiation chemical yield ‘g value’ is generally reduced. For e.g., in Fricke at very high dose rate the g value is reduced, which if not corrected for may lead to erroneous results. For commercial purposes, the commodity to be radiation processed moves in a designated path in an irradiator with varying dose rates. The dose rate study helps to establish a dosimeter for use in radiation processing facility. In the present study, the dosimeters are irradiated using different dose rate irradiation facilities. Dose values are compared with each other and any correction to be applied is suggested.

2.11.3 Effect of dose fractionation

In radiation processing facilities, breakdowns are faced due to power shutdown, mechanical failures or other such problems. Due to such events there is a gap between the total dose received. Dosimeters are irradiated with different time gaps to simulate the effect. Single dose is given in two equal fractions or 3-4 small equal fractions to provide same total dose with varying time intervals. In low range dosimeters, this effect is more profound. In general, low dose dosimeters are highly dependent on dose fractionation effect and generally not useful for such studies. Different time gaps are provided to deliver same dose with different dose fractions. The value are compared to dose values without fractionation and based on the results, effect of dose fractionation is provided.

2.11.4 Time dependence study

Free radicals generated during irradiation react with the reactants at fast rates especially in aqueous systems. However molecular products like hydrogen peroxide have slow reaction rate and it takes long time for its reactions to complete. For this reason Fricke dosimeters are measured at least 15 minutes after irradiation. In non-aqueous systems, for e.g. radiochromic films, the colour development continues for few hours after irradiation. To counter this effect the films are subject to thermal treatment prior to absorbance measurement. Apart from this, there can be some other inherent reactions in the system that may lead to increase/decrease in signal intensity. Time course study provides the time frame for carrying out measurements beyond which it is not recommended for accurate dose measurements. In this study the dosimeters are irradiated and measured as quickly as possible. The variation with time is recorded and the results provide optimum time frame of measurement.

2.11.5 Reproducibility study

It is extremely important for any dosimetry system to be reproducible. The degree of reproducibility along with other uncertainties involved decides the usability of the dosimeter.

For a system to be working as a dosimeter, it is very important for it to have low degree of variation and high degree of reproducibility. In general it is found that at low doses the reproducibility is higher compared to that observed at higher doses. This is due to masking of small variations in high dose values. The reproducibility study is carried out by irradiating two sets of dosimeters so as to cover the upper and lower range of dosimeter under study.

Their signal intensity for e.g. absorbance is recorded and variation is observed for 5-10 such dosimeters depending on the range.

2.11.6 Pre- and post- irradiation stability

For any dosimeter, its stability decides its usefulness especially while using in field. Before irradiation the dosimeter is subjected to environmental effects such as humidity, light, temperature fluctuations, and leaching chemicals of container. In addition to this, the dosimeters can undergo autocatalytic changes that may lead to increase or decrease of signal intensity prior to its use. Although control or blank provides value of change occurred, a better understanding is obtained by proper study. Thus, the dosimeters solution is preferably stored in glass vessels as it shows minimum leaching towards chemicals. The solutions are then kept in dark environment under laboratory conditions and separately in refrigerated conditions. The solutions are then irradiated to known doses in gamma chambers. Variation in values of signal intensity indicates their time and condition for usefulness as dosimeters. For e.g. Fricke dosimeters once prepared can be used upto 1 month if kept refrigerated, while perspex dosimeters have shelf life of more than 10 years. Molecular products and some free radicals have slow reactions and tend to linger on for a long time after irradiation is complete. Owing to these and other effects like rearrangement there is small change in the signal intensity with time after irradiation. The post irradiation stability for liquid systems is generally expected upto a day. While for solid systems the post irradiation stability can go up for months. For e.g. in Alanine pellets the free radicals formed due to irradiation are stable for years together with 1% decrease in signal intensity reported annually. This is not exhaustive list of studies other effects being; LET Effect, Effect of stabilizers on stability, Humidity effect (not applicable for aqueous solutions)

2.12 Calculation of absorbed dose using chemical dosimeters

Beer-Lambert's Law: $\mathbf{A = \log (I_0/I) = \varepsilon CL}$

Where, A = absorbance, I_0 = intensity of light incident upon sample cell, I = intensity of light leaving sample cell, C = molar concentration of solute, L = length of sample cell (cm.), ε = molar absorptivity, Transmittance $T = I / I_0$,Net absorbance (ΔA)

$\mathbf{\Delta A = | A_i - A_o |}$

$\mathbf{\Delta A = \varepsilon \Delta C L}$

G(X) is the radiation chemical yield of X formed or destroyed in mol per unit energy absorbed in Joule

$\mathbf{G (X) = n (x) / E}$(mol J^{-1})

$\therefore \mathbf{E = n (x) / G (X) \quad (J\ m^{-3})}$

If ΔC mol m^{-3} is the concentration of this product formed during radiolysis,

$\therefore$Energy absorbed, $\mathbf{E = \Delta C / G (X)}$ J m^{-3}

However, unit of absorbed dose, Gy is in J kg^{-1}

$\therefore \mathbf{Dose = \Delta C / G (X) \times \rho}$

Where, ρ = density (kg m^{-3}) of the dosimetric solution.

Now since, $\mathbf{\Delta A = \varepsilon \Delta C L}$ [According to Beer-Lambert's Law]

$\therefore \mathbf{\Delta C = \Delta A / \varepsilon \times L}$

$\therefore \mathbf{Dose = \Delta A / \{G (X) \times \varepsilon \times \rho \times L\}}$

Where, ε is the molar linear absorption coefficient of the product at the wavelength used for spectrophotometric measurements and L is the optical path length. ρ is the density of the solution in kg/m^3

2.12.1 Calculation of absorbed dose in a material

For electromagnetic radiation, when both the dosimeter and the material are exposed to the same radiation field and are in electronic equilibrium, the dose in the dosimeter (D_d) and the material (D_m) are related by,

$$\mathbf{D_m = D_d \ x \ (\mu_{en}/\rho)_m / (\mu_{en}/\rho)_d} \qquad \text{Gy}$$

Where, $(\mu_{en}/\rho)_m$ and $(\mu_{en}/\rho)_d$ are mass energy absorption coefficients for the dosimeter and the material respectively.

For compounds and mixtures the mass energy absorption coefficients are combined in proportion to their weight in sample to obtain an average value, which can be substituted in the earlier equation.

Table 2.3: Mass energy absorption coefficient (μ_{en}/ρ) in m^2kg^{-1} for Cobalt-60 gamma rays

Material	(μ_{en}/ρ)	Material	(μ_{en}/ρ)
H	5.309×10^{-3}	Pb	3.240×10^{-3}
C	2.666×10^{-3}	Air	2.662×10^{-3}
N	2.666×10^{-3}	Water	2.961×10^{-3}
O	2.666×10^{-3}	Polystyrene $(C_6H_6)n$	2.871×10^{-3}
P	2.580×10^{-3}	Lucite (Perspex) $(C_5H_8O_2)n$	2.879×10^{-3}
S	2.655×10^{-3}	Polyethylene $(CH_2)n$	3.046×10^{-3}
Ar	2.390×10^{-3}	Bakelite $(C_{43}H_{38}O_7)n$	2.818×10^{-3}
K	2.585×10^{-3}	Amber $(C_{10}H_{16}O)n$	2.946×10^{-3}
Al	2.570×10^{-3}	0.8N H_2SO_4	2.945×10^{-3}
Fe	2.495×10^{-3}	Pyrex glass	2.645×10^{-3}
Cu	2.455×10^{-3}	Muscle	2.931×10^{-3}

In the range of photon energies in which interaction is predominantly by Compton process, the equation, $\mathbf{D_m = D_d \ x \ (\mu_{en}/\rho)_m / (\mu_{en}/\rho)_d}$ can be simplified to

$$\mathbf{D_m = D_d \ x \ (Z/A)_m / (Z/A)_d} \text{Gy (Attix 2007)}$$

2.13 Concept of Buildup and its importance in dosimetry

Absorbed dose is a physical dose quantity D representing the mean energy imparted to matter per unit mass by ionizing radiation. In the SI system of units, the unit of measure is joules per kilogram, and its special name is gray (Gy). KERMA is an acronym for "kinetic energy released per unit mass", defined as the sum of the initial kinetic energies of all the charged particles liberated by uncharged ionizing radiation (i.e., indirectly ionizing radiation such as photons and neutrons) in a sample of matter, divided by the mass of the sample. The SI unit of kerma is the gray (Gy) (or joule per kilogram), the same as the unit of absorbed dose. However, Kerma dose is different from absorbed dose, according to the energies involved, partially because ionization energy is not accounted for. KERMA is the expectation value of the energy transferred to the charged particles per unit mass at a point of interest, including radiative-loss energy but excluding energy passed from one charged particle to another.The kerma for x- or gamma-rays consists of the energy transferred to electrons and positrons per unit mass of medium. The kinetic energy of a fast electron may be spent in two ways: Coulomb-force interactions with atomic electrons of the absorbing material, resulting in the local dissipation of the energy as ionization and excitation in or near the electron track. These are called ***collision*** interactions. Radiative interactions with the Coulomb force field of atomic nuclei, in which X-ray photons (bremsstrahlung, or “braking radiation”) are emitted as the electron decelerates. These x-ray photons are relatively penetrating compared to electrons and they carry their quantum energy far away from the charged-particle track. In addition, a ***positron*** can lose an appreciable fraction of its kinetic energy through in-flight annihilation, in which the kinetic energy possessed by the particle at the instant of annihilation appears as extra quantum energy in the resulting photons. Hence, this is also a type of radiative loss of kinetic energy, in which the resulting photons can carry kinetic energy away from the charged-particle track. Since the kerma includes kinetic energy received by the charged particles whether it is destined to be spent by the electrons in collision or radiative-type interactions, we can subdivide K into two parts according to whether the energy is spent nearbyin creating excitation and ionization (K_c) or is carried away by photons (K_r)

$$K=K_c+K_r$$

Where, the subscripts refer to ‘‘collision” and “radiative” interactions, respectively.

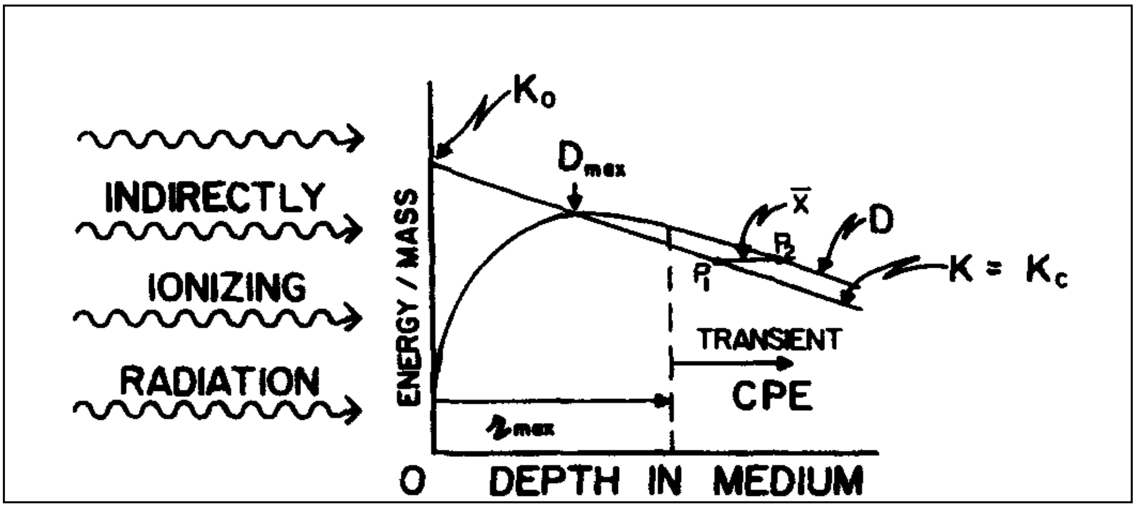
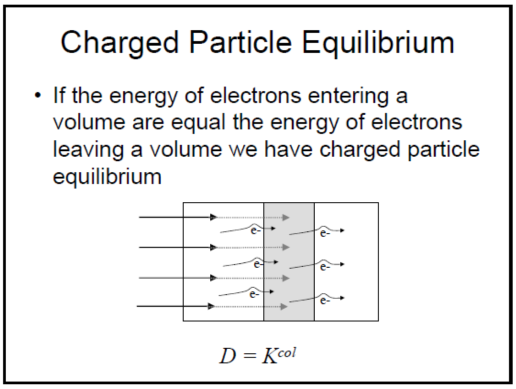


Figure 2.12: Transient Charged Particle Equilibrium

Figure 2.12 illustrates Transient Charged Particle Equilibrium for high energy indirectly ionizing radiation incident from the left on a slab of material. Radiative losses are assumed to be absent, so Kr = 0 and K= K_c (Hölm 1969), (Attix 2007). The absorbed-dose curve is shown rising with increasing depth near the surface as the population of charged particles flowing toward the right is augmented by more and more interactions of indirectly ionizing rays. The dose curve reaches a maximum (D_{max}) at the depth where the rising slope due to buildup of charged particles is balanced by the descending slope due to attenuation of the indirectly ionizing radiation. For a “clean” beam of indirectly ionizing radiation D_{max} occurs at approximately the same depth as where the Dose-curve D crosses the K_c (collision KERMA)-curve. However, the presence of charged-particle “contamination” in the beam is often observed to shift the depth of D_{max} closer to the surface, where it no longer approximates the depth at which $D = K_c$ (Biggs and Ling 1979). Thus, one should not assume that $D = K_c$, at D_{max}. At a somewhat greater depth $\boldsymbol{r}_{max}$, equal to the maximum distance the secondary charged particles starting at the surface can penetrate in the direction of the incident rays, the D-curve becomes parallel to the K_c-and K (KERMA)-curves, although all may gradually change slope together with depth. D therefore becomes proportional to K_c , and we say that TCPE (Transient Charged Particle Equilibrium) exists. In radiological physics, charged-particle equilibrium (CPE) occurs when the number of charged particles leaving a volume is equal to the number entering, for each energy and type of particle. When CPE exists in an irradiated medium, the absorbed dose in the volume is equal to the collision kerma.

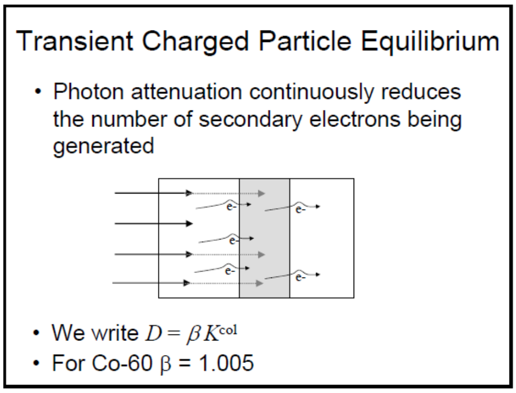


Charged Particle Equilibrium

- If the energy of electrons entering a volume are equal the energy of electrons leaving a volume we have charged particle equilibrium

$D = K^{col}$

Figure 2.13: Charged Particle Equilibrium



Transient Charged Particle Equilibrium

- Photon attenuation continuously reduces the number of secondary electrons being generated

- We write $D = \beta K^{col}$
- For Co-60 β = 1.005

Figure 2.14: Transient CPE

In actual cases, photon attenuation continuously reduces the number of secondary electrons being generated this is called Transient Charged Particle Equilibrium. Dosimetry is best performed in region of Charged Particle Equilibrium as the uncertainty arising due to contribution of dose by electrons from surface of container holding dosimeter solution is the least. For this reason,solution containers are placed in perspex build-up to provide required wall thickness for attaining electronic equilibrium during irradiation. For ^{60}Co gamma radiations the buildup thickness is (400 mg/cm^2) that equals to 4 mm of perspex with density 1.2 g/cc. The value 400 mg/cm^2 is the range of electrons with energy 1.33 MeV. As the maximum energy of electrons generated by ^{60}Co gamma radiations can be 1.33 MeV (photoelectric effect), value of its range is taken as buildup thickness for ^{60}Co gamma irradiations.

Many analytical techniques exist for analyzing chemical dosimeters such as, Electron Paramagnetic Resonance Spectrometry, Potentiometry, Colourimetry, Polarimetry, and Spectrophotometry.

2.14 UV-Visible Spectrophotometry

A spectrophotometer can be either single beam or double beam. In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. The reference beam intensity is taken as 100% Transmission (or 0 Absorbance), and the measurement displayed is the ratio of the two beam intensities. Samples for UV/Vis spectrophotometry are most often liquids, although the absorbance of gases and even of solids can also be measured. Samples are typically placed in a transparent cell, known as a cuvette. Cuvettes are typically rectangular in shape, commonly with an internal width of 1 cm. The most widely applicable cuvettes are made of high quality fused silica or quartz glass because these are transparent throughout the UV, visible and near infrared regions. A complete spectrum of the absorption at all wavelengths of interest can be produced directly by the spectrophotometer. Jasco V-530 UV/Vis double beam spectrophotometer (Figure 2.15) has been used for all absorbance measurements reported in this thesis.

Figure 2.15: Jasco V-530 UV/Vis double beam spectrophotometer

2.15 Principle of Electron Paramagnetic Resonance (EPR) Spectroscopy

When a molecule or compound with an unpaired electron is placed in a strong magnetic field, the spin of the unpaired electron can align in two different ways creating two spin states, $m_s = \pm \frac{1}{2}$. The alignment can either be along the direction (parallel) to the magnetic field which corresponds to the lower energy state $m_s = -\frac{1}{2}$ or, opposite (antiparallel) to the direction of the applied magnetic field $m_s = +\frac{1}{2}$. The two alignments have different energies and this difference in energy lifts the degeneracy of the electron spin states. The energy difference is given by:

$\Delta E = E+ - E- = h\nu = gm\beta B$

Every electron has a magnetic moment and spin quantum number, $s=1/2$ with magnetic components $m_s = +1/2$ and $m_s = -1/2$. In the presence of an external magnetic field with strength, B_0, the electron's magnetic moment aligns itself either parallel ($m_s = -1/2$) or antiparallel (m_s = +1/2) to the field, each alignment having a specific energy due to the Zeeman effect :

$E = m_s g_e \mu_B B_0$

Where, g_e is the electron's so-called g-factor (see also the Landé g-factor).g_e = 2.0023 for the free electron (https://en.wikipedia.org/wiki/Electron_paramagnetic_resonance#cite_note-1 n.d.). μ_B is the Bohr magneton.

Therefore, the separation between the lower and the upper state is $\Delta E = g_e \mu_B B_0$ for unpaired free electrons. This equation implies that the splitting of the energy levels is directly proportional to the magnetic field's strength, as shown in Figure 2.16.

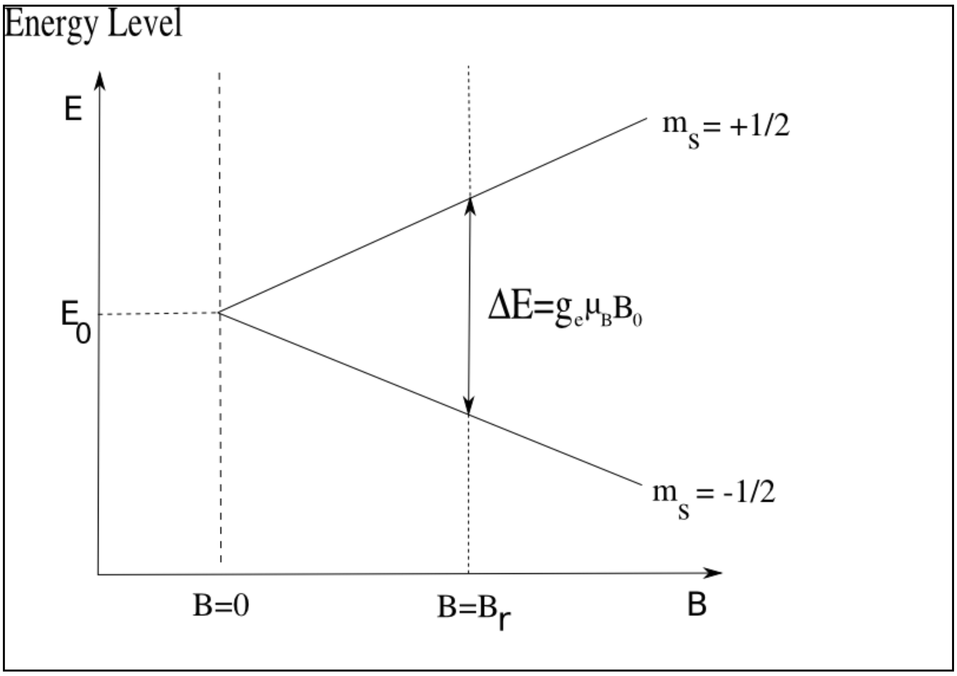


Figure 2.16: Splitting of the unpaired electrons' energy levels

h = Planck's constant (6.626×10^{-34} J s^{-1}),

ν = the frequency of radiation,

β = Bohr magneton (9.274×10^{-24} J T^{-1}),

B = strength of the magnetic field in Tesla,

g = the Landé g-factor (Proportionality factor)

During the experiment, the values of h, v, and β does not change and g value decrease as B increases. The g-factor is a unitless measurement of the intrinsic magnetic moment of the electron, and its value for a free electron is 2.0023. The concept of g can be roughly equated to that of chemical shift in NMR. EPR spectrum is the absorption of microwave frequency radiation plotted against the magnetic field intensity (Weil and Bolton 2011).

In an EPR experiment the field of the spectrometer magnet is swept linearly to excite some of the electrons in the lower energy level to the upper energy level while the sample is exposed to fixed microwave irradiation. The free or the unpaired electrons have a small magnetic field and orient themselves parallel to the larger field produced by the spectrometer's magnet. At a particular magnetic field strength the microwave irradiation will cause some of the free electrons to "flip" and orient against the spectrometer's magnetic field. This separation between the lower and the higher energy level is exactly matched by our microwave frequency. The condition where the magnetic field and the microwave frequency are "just right" to produce an EPR resonance (or absorption) is known as the resonance condition is detected by the spectrometer. EPR spectroscopy can be carried out by either varying the magnetic field and holding the frequency constant or, varying the frequency and holding the magnetic field constant (as is the case for NMR spectroscopy). Typically, a commercial spectrometer works by varying the magnetic field and holding the frequency constant. EPR spectrometers working at frequencies ranging from several hundred MHz to several hundred GHz are in use, such as, 1-2 GHz (L-band) and 2-4 GHz (S-band), 8-10 GHz (X-Band), 35 GHz (Q-band) and 95 GHz (W-band). The most commonly used EPR spectrometer is in the range of 9-10 GHz (X-band).Measuring a CW-EPR spectroscopy can be influenced by various parameters, both instrumental and experimental. The significant aspect of the measurement is to get a high resolved EPR spectrum from a low concentration sample of interest which is dependent on the sensitivity and the resolution of the spectrometer. Microwave bridge and Resonator governs the sensitivity of the signal. Magnet, Magnet field controller, Magnet power supply and signal channel control the resolution of the spectrum obtained.

Alanine EPR is only direct method to detect the presence of free radicals and to identify the paramagnetic species Provides information on molecular structure near the unpaired electron.

EPR spectra line shape gives insight to dynamic processes molecular motions or fluidity, probes the structure of “active sites” in metalloproteins and dose measurements for sterilization of medical goods and foods, detection of irradiated foods, and the dating of early human artifacts (Banwell 1994).

Figure 2.17: EPR spectrometer

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 and energy and is relatively insensitive to temperature and humidity. Thus, alanine dosimetry is equally suited to Gamma, E-beam, or X-ray irradiation facilities. Alanine dosimeters are available as pellets or films depending on the application. The advantages of alanine dosimetry are:

1% accuracy or better

Dose rate independent

Detection limit below 1 Gray

Accurate from 10 Gray to 200 kGy

Bar code reader for sample archiving

Compatible with ASTM E1607

Alanine EPR spectrometer available for standardization and calibration of dose and dosimeters at Chemical Dosimetry Lab, RSSD, BARC is shown in Figure 2.17.

2.16 Calibration of spectrophotometer

Requisites

UV double beam spectrophotometer

Reagents (Analytical grade):

Potassium dichromate, Potassium chloride, Potassium nitrate, Single distilled water, Six 100 ml standard volumetric flasks, One 1000 ml standard volumetric flask, 10 ml graduated pipette, Holmium oxide imbedded in glass matrix, Stainless steel spatula, Two 5 ml beakers Semi-micro weighing balance, lint free tissue papers, Optical cuvettes with 10 mm pathlength.

Method

2.16.1 Control of absorbance

The absorbance is checked using solution of potassium dichromate (0.060 g L^{-1}) in dilute sulphuric acid (5 mol m^{-3}) at the wavelengths indicated in Table 2.4, with 5 mol m^{-3} sulphuric acid as the reference solution. Table 2.4 gives for each specified wavelength the exact value of A (1%, 1 cm) and the permitted limits. A (1%, 1cm) = A / c l where, A is the absorbance at the specified wavelength c is the concentration of the absorbing substance expressed as percentage w / v and l is the thickness of the absorbing layer in cm. The value of A (1%, 1cm) at a particular wavelength in a given solvent is a property of the absorbing substance.

Table 2.4: Absorbance and maximum tolerance at specified wavelengths for dichromate

Wavelength (nm)	A (1%, 1cm)	Maximum tolerance
235	124.5	122.9 to 126.2
257	144.0	142.4 to 145.7
313	48.6	47.6 to 50.3
350	106.6	104.9 to 108.2

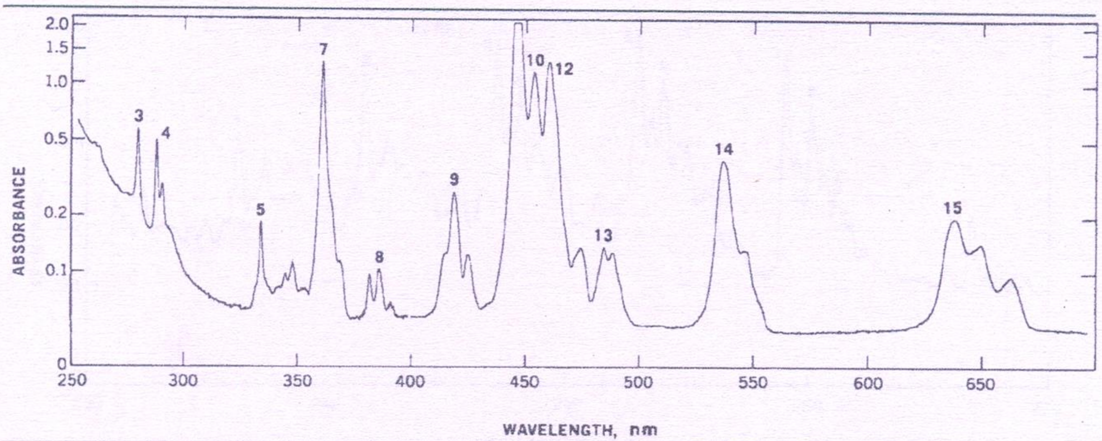
2.16.2 **Determination of wavelength accuracy**

The holmium oxide glass filter or solution standard (4% mass fraction holmium oxide in 10% volume fraction perchloric acid) contained in a 10 mm pathlength cuvette may be used for evaluating wavelength accuracy (Figure 2.18). Absorbance maxima or transmittance minima must be located within ± 1 nm of the wavelengths given below (Table 2.5):

Table 2.5: Calibration wavelengths for Holmium Oxide standards

 Holmium Oxide Glass Filter	Glass filter	Solution
	241.5 nm	241.1 nm
	279.3 nm	278.1 nm
	287.6 nm	287.2 nm
	333.8 nm	333.4 nm
	360.8 nm	361.3 nm
	418.5 nm	416.3 nm
	459.9 nm	467.8 nm
	536.4 nm	536.6 nm
	637.5 nm	640.5 nm

If the observed absorption bands of the holmium oxide glass or solution deviate by more than ± 1 nm from the values stated, then corrective service must be performed on the instrument by a qualified service person.

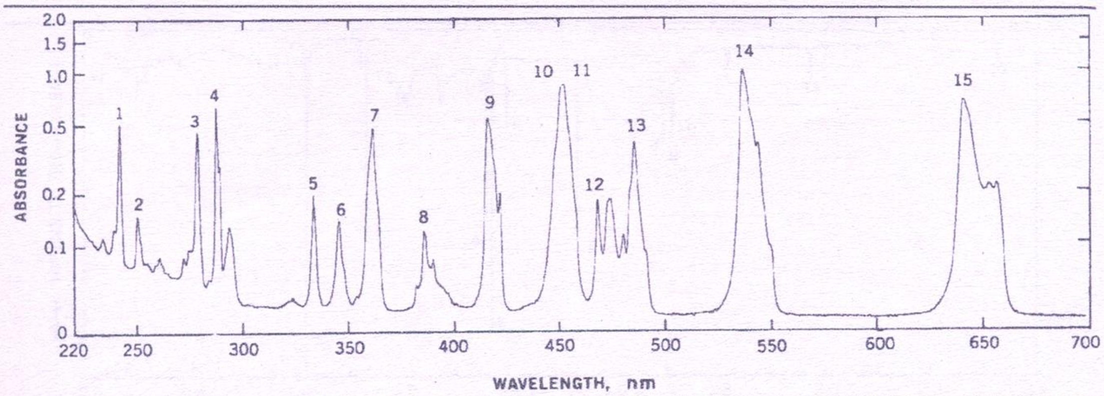


Band Number	Wavelength, nm	Band Number	Wavelength, nm	Band Number	Wavelength, nm	Band Number	Wavelength, nm
3	279.4	7	360.9	10	453.2	14	536.2
4	287.5	8	385.9	12	460.0	15	637.5
5	333.7	9	418.7	13	484.5		

Instrument: Cary Model 14
Scanning Speed: 10A/s
Slit Width: 0.025 to 0.105 mm

Spectral Slit Width: 0.10 to 0.40 nm
Sample Thickness: 2.6 mm

FIG. 2 Spectrum of Holmium Oxide Glass Showing Reference Wavelength (5)



Band Number	Wavelength, nm	Band Number	Wavelength, nm	Band Number	Wavelength, nm	Band Number	Wavelength, nm
1	241.1	5	333.4	9	416.3	13	485.8
2	249.7	6	345.5	10	450.8	14	536.4
3	278.7	7	361.5	11	452.3	15	641.1
4	287.1	8	385.4	12	467.6		

Instrument: Cary Model 14
Scanning Speed: 10A/s
Slit Width (Visible): 0.02 to 0.10 mm
(Ultraviolet): 0.09 to 0.40 mm

Spectral Slit Width (Visible): 0.1 to 0.4 nm
(Ultraviolet): 0.3 to 0.7 nm
Reference: 1.4 *M* Perchloric acid in 1-cm cell

FIG. 3 Spectrum of 4 Percent Solution of Holmium Oxide in 1.4 *M* Perchloric Acid (1.00-cm Cell) Showing Reference Wavelengths (5)

Figure 2.18: Spectrum of Holmium Oxide in solution form

2.16.3 **Limit of stray light**

Stray light may be detected at a given wavelength with suitable filters or solutions, for example, the absorbance of a 1.2% w / v solution of potassium chloride at a pathlength of 10 mm should be greater than 2.0 at about 200 nm when compared with water as reference liquid.

2.16.4 **Linearity test for absorbance**

Different concentrations of potassium nitrate are prepared in 100 ml standard volumetric flasks, viz 0.5 % w/v, 1.0 % w/v, 1.5 % w/v, 2.0 % w/v and 2.5 % w/v in single distilled water. The absorbance of these solutions is measured using 10 mm pathlength cuvette with water as the reference at 303 nm. A graph of absorbance vs. concentration of potassium nitrate is plotted. This graph should be a straight line passing through the origin. Any divergence form this pattern indicates non-linearity in absorbance measurement of the spectrophotometer used.

If all the above test results are within the criteria specified then the spectrophotometer is said to be calibrated and functioning properly (ASTM E925-09(2014) 2014).

2.17 Calibration of irradiation equipment

Calibration of irradiation equipment is done by performing regular dosimetry exercises. Procedure for Calibration of a Cobalt-60 Gamma Chamber using Fricke Dosimetric System is discussed in brief.

Fricke dosimeter or the ferrous sulphate dosimeter is the best known and extensively used chemical dosimeter. It provides a reliable means for measurement of absorbed dose in the range 20 to 400 Gy and is widely accepted because of its accuracy and reliability. It is classified as a reference standard dosimeter. When an air saturated dilute ferrous sulphate or ferrous ammonium sulphate solution in 400 mol. m^{-3} sulphuric acid is exposed to ionizing radiation, ferrous ions are oxidized to ferric ions. The oxidation of ferrous ions is directly proportional to the dose. Fricke dosimetric solution is composed of 1 mol m^{-3} ferrous ammonium sulphate, and 1 mol m^{-3} sodium chloride in 400 mol m^{-3} sulphuric acid. This solution is prepared in aerated single distilled water. Before filling the Fricke solution, the polypropylene irradiation tubes are filled with 10 % aqueous nitric acid kept for 24 hrs. After washing them thoroughly with distilled water, the tubes are filled with distilled water and irradiated to a dose of about 100 Gy. 15 such pre-cleaned polypropylene tubes are rinsed with Fricke solution at least for three times before filling. Care should be taken not to touch the inside of the tube or stopper while filling it. It should also be seen that no air bubble is trapped inside while stoppering the tubes.

An irradiation set-up is used for providing reproducible irradiation geometry for irradiating Fricke dosimeters at the center of the irradiation volume of the gamma chamber. Irradiation set-up for calibration of the gamma chamber is as shown in Figure 2.19.

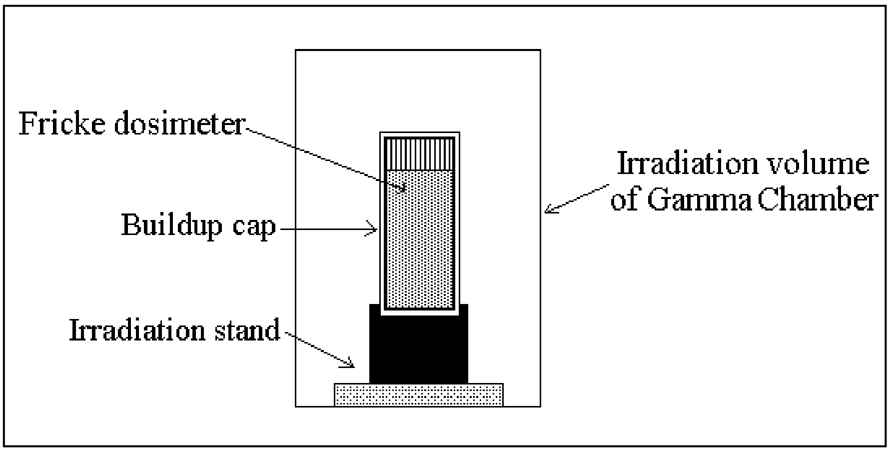


Figure 2.19: Irradiation set-up for calibration of gamma chamber

2.17.1 **Analytical technique**

Spectrophotometers are calibrated as discussed in section 2.15. The wavelength is adjusted to 303 nm. The 10 mm quartz cuvette is cleaned with distilled water. Without inserting the quartz cuvette in the spectrophotometer, 0 % and 100 % transmission are adjusted against air as reference. Quartz cuvette is rinsed twice with distilled water and filled with solution to be analyzed. The cuvette is placed in the sample compartment and its absorbance noted. The quartz cuvette is rinsed with Fricke solution from the control, at least twice and filled. After filling, it is placed in the sample compartment. The absorbance (A_c) of control (unirradiated) dosimeters and irradiated dosimeters (A_{irr}) are measured against air as reference. The zero balance is checked after each solution is measured with only air in the light paths. Periodically, during the measurement process, the absorbance of distilled water is remeasured to detect any contamination of the cuvette and appropriate corrective actions are made, if required. The temperature of the sample solution (irradiated dosimeter) is measured carefully, using a 50 °C thermometer (having up to 1/10th of the graduation). Average absorbance of control dosimeters (A_c) is calculated and the net change in absorbance ΔA ($\Delta A = A_{irr} - A_c$) for each irradiated dosimeter is determined. The results are tabulated as indicated in Table 2.6, Table 2.7 and Figure 2.20.

2.17.2 **Calculation of absorbed dose**

The basic equation for calculation of absorbed dose in the dosimetric solution is as follows:

$$D_F = \Delta A / (\varepsilon\ G\ \rho\ d) \qquad \ldots\ldots\ldots\ldots..(1)$$

Where,

D_F = Absorbed dose in Fricke solution, Gy

ΔA = Net change in absorbance at 304 nm

ε = Molar linear absorption coefficient, $m^2\ mol^{-1}$

ρ = Density ($1024\ kg\ m^{-3}$) of Fricke solution

d = Optical pathlength (0.01 m) of dosimetric solution,

To calculate the absorbed dose in water (ASTM E 1026), use the equation,

$D_W = 1.004\ D_F$ ………………..(2)

Hence, $D_w = (1.004\ (\Delta A)) / (\varepsilon\ G\ \rho\ d)$ ……….........(3)

ICRU 35 (ICRU 35 1984) recommends the use of the product εG in the equation (1) rather than individually determined values of ε and G. The recommended value of ε G is 352×10^{-6} $m^2\ J^{-1}$ for absorbance measurement temperature of 25 °C. Both ε and G have temperature coefficients as 0.7 % and 0.15 % per ° C. Hence, value of εG must be corrected for temperature and substituted in the equation (1)

$\varepsilon G = 352 \times 10^{-6}\ [\ 1 + 0.007\ (t - 25)] \times [\ 1 + 0.0015\ (\ t' - 25\ )\ ]$ ………..(4)

Where,

t = temperature (°C) of dosimetric solution during spectrophotometric measurement, that affects the value of ε.

t’ = temperature (°C) of irradiation, which affects G value.

Combining equations (3) and (4),

$D_w = 1.004\ (\Delta A)\ /\ [352 \times 10^{-6}\ (1 + 0.007\ (t - 25)) \times (1 + 0.0015\ (t' - 25)) \times 1024 \times 0.01]$

………………………………(5)

Equation (4) is valid for an irradiation temperature range of 10 - 60 °C and absorbance measurement temperature range of 10 - 35 °C.

2.17.3 Experimental Data for Calibration of Gamma Chamber – 1200 (RSSD)

Date of calibration: 21.05.15

Irradiation geometry: Center Bottom

Dosimeter used: Fricke dosimeter

Dosimetry procedure: (ISO/ASTM 51026:2015 2015)

Measurement temperature : 25.6 ^oC

Temperature during irradiation : 28.2 ^oC

Wavelength for maximum absorption: 304 nm

Pathlength : 1 cm (10 mm)

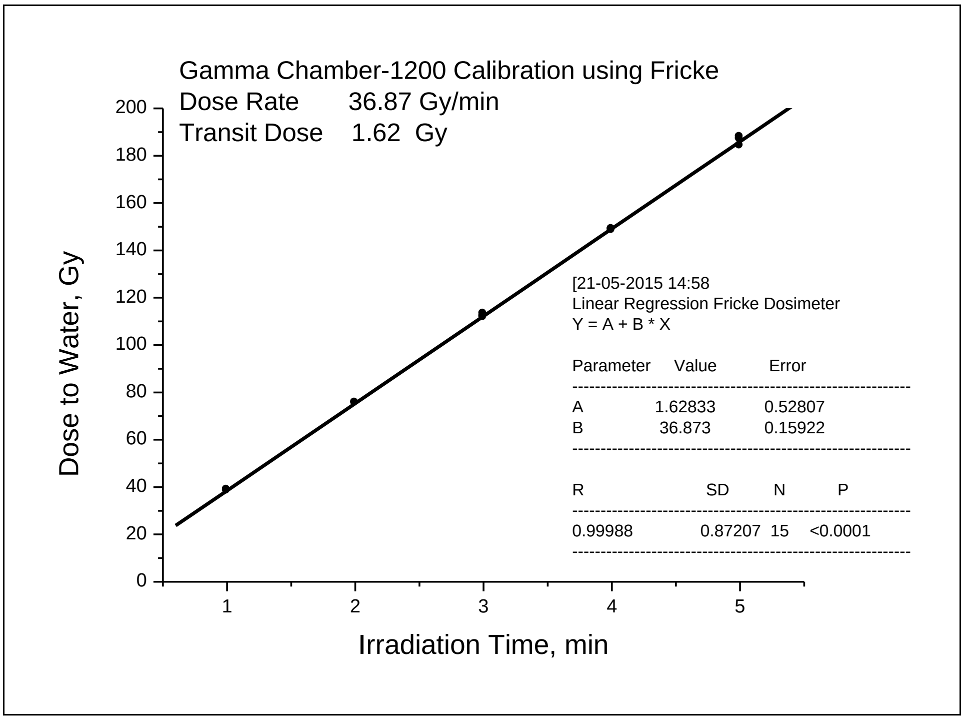
Spectrophotometer used : Jasco V530 UV/Vis

Table 2.6: Absorbance values of unirradiated (Control) solutions

Control solution No.	Abs.
B1	0.059
B2	0.058
B3	0.059
B4	0.058
B5	0.061
Avg. abs.	0.059

Table 2.7: Absorbed Dose (Gy) calculated using Fricke dosimeter

Sample No.	Irradiation time, min	Abs.	Net Abs.	Dose Gy
1	1	0.198	0.139	38.48
2	1	0.198	0.139	38.32
3	1	0.200	0.141	38.79
4	2	0.333	0.274	75.53
5	2	0.332	0.273	75.42
6	2	0.332	0.273	75.42
7	3	0.469	0.410	113.1
8	3	0.463	0.404	111.61
9	3	0.465	0.406	112.16
10	4	0.598	0.539	148.82
11	4	0.597	0.538	148.38
12	4	0.598	0.539	148.82
13	5	0.726	0.667	184.1
14	5	0.736	0.677	186.91
15	5	0.740	0.681	187.85



```
[21-05-2015 14:58
Linear Regression Fricke Dosimeter
Y = A + B * X

Parameter     Value         Error
------------------------------------------------------------
A             1.62833       0.52807
B              36.873       0.15922
------------------------------------------------------------

R                  SD       N      P
------------------------------------------------------------
0.99988          0.87207  15    <0.0001
------------------------------------------------------------
```

Figure 2.20: Gamma chamber dose calibration graph

Another dosimetry system used by RSSD, BARC for calibration of other dosimeters and irradiation devices is the Alanine EPR spectrometer. Gamma chambers are calibrated by using procedures similar to that explained earlier for Fricke dosimeters. Alanine EPR procured from Bruker, Germany is fully automated system. The alanine dosimeters in the form of pellets for gamma and films for electron beam are irradiated for different time to provide dose. The dose values are compared with the dose values of calibrated dosimeters supplied by Standard Laboratories like National Physical Laboratory, UK and National Institute of Standards and Technology, USA to evaluate the variation involved between the values. Its general working principle and theory are discussed in the succeeding part. (Protocol followed by Chemical Dosimetry Group, RSSD, BARC)

2.18 Cleaning procedures

Glasswares

Glasswares are filled with a mixture of 1:1 concentrated sulphuric acid and nitric acid for 24 hours in fumehood. They are washed thrice with single distilled water. In addition to acid cleaning, distilled water-filled glasswares are irradiated to a dose of about 100 Gy. Finally they are washed thrice with distilled water (ASTM C912-93 2013)

Non glass equipment

All other non-glass equipment such polyethylene wash bottles, polypropylene tubes, dosimeter containers and polyethylene bags should be filled with 10 % aqueous nitric acid for 24 hrs. They are washed thrice with distilled water. Polypropylene tubes used for dosimetry should be rinsed with solution to be irradiated and are filled with the same. Dosimeter solution should be kept filled in the tubes for at least 15 days to achieve proper conditioning of the tube. Reason for choosing polypropylene tubes is the least leaching effect observed during irradiation among commonly available polymers (Gupta and Narayan 1974), (Gupta, Bhat and Narayan, et al. 1985).

2.19 Other instruments used in the study

Single Distillation Unit Quartz (Distillation Of Water) LABSIL India, Output capacity 2 litres per hour,1.5 kW single phase unit is used for collecting Single distilled water which was used in all experiments. Sartorius balance is used for all weight measurements, having least count of 0.1 mg. The list of other equipment and instruments used are stop watch, pH meter, humidity meter, heating mantle, thermometer etc. TLDs used for personal dose monitoring were worn while performing irradiations. All calculations were done using Microsoft Excel; graphs were plotted using ORIGIN 6.0 software.

Chapter 3 Development of New Chemical Dosimeter for Low Dose Range: Ferrous Sorbitol Xylenol Orange Dosimeter

3.1 Introduction

Several solid and liquid systems are available for low dose dosimetry. Alanine ESR readout method (ASTM 51540 2004) provides a promising answer with high accuracy for measuring therapy level radiation doses and is used widely for dose inter-comparison exercises (Lin M. and et.al. 2010) however, the high cost restricts their use as a dosimeter for routine purposes. Although ionization chambers provide highest precision (TRS-398 2000), its online measurement system and associated electronics limits their use in small irradiation facilities such as gamma chambers and blood irradiators, generally used for experimental radiation biology studies. Solid luminescence based reusable dosimeters such as RPL, OSL and TL with easy readout are cheaply available (Olko 2010) although considerably high effective atomic number of some dosimeters affects the electronic equilibrium for*in situ* measurements. Film dosimeters such as Gafchromic films are suitable for the measurement of high resolution dose distributions with the depth, radiation dose mapping and radiographic imaging (McLaughlin, Chen and Soares 1991); (McLaughlin 1993) due to their extremely high spatial resolution and good reproducibility.

However, liquid systems occupy complex volumes providing them an upper hand over the solid systems especially in radiation biology based applications. Radiochromic liquid dosimetry systems (ASTM 51540 2004) have been successfully used for radiation biology applications. However, their chemical composition makes it difficult for *in vivo* measurements and similar applications.

Benzoic acid in aqueous media has been found to enhance the oxidation of ferrous ions thus, acting as radiolytic sensitizer for the ferrous based system i.e. Fricke. A sensitive chemical dosimetric system consisting of a dilute solution of ferrous ammonium sulphate in dilute sulphuric acid, containing benzoic acid and a dye xylenol orange was developed at BARC. Ferrous ions, in acidic medium, get oxidized to ferric ions when exposed to ionizing radiation.

$$Fe^{2+} \text{\^{}\^{}\^{}\^{}\^{}\^{}\^{}\^{}\^{}-}> Fe^{3+}$$

Presence of organic compound such as benzoic acid increases the radiolytic oxidation of ferrous ions (E.J.Hart,1952), thereby increasing the radiation chemical yield of ferric ion formation.This extends its lower limit of detection with highly reproducible results (Gupta and Nilekani 1998). Xylenol orange specifically complexes with ferric ions in 1:1ratio (Gay and Gebicki 1999) under acidic conditions (Gay, J. and J.M. 1999) providing analytical sensitivity to the dosimeter, thus further enhancing the lower limit of detection. Sorbitol enhances the oxidative action of peroxides in FX solution (Gay and Gebicki 2000). In Glycine–FX spectrophotometric readout method (Shinde and Mukherjee, Gamma dose measurement by glycine system using spectrophotometric readout method 2006) ferrous ion oxidation has been shown to be enhanced in presence of sorbitol (Shinde and Mukherjee 2009). Therefore, sorbitol was tried as a readily soluble organic compound, as compared to benzoic acid, to sensitize the ferrous based system i.e. Fricke, by enhancing the oxidation of ferrous and complexing the ferric ions thus formed using xylenol orange that is also found to control the chain length of free radical reactions (Gupta, Bhat and Narayan, et al. 1985)

Xylenol orange forms a 1:1 complex with ferric ions. It has an absorption maximum in the visible region. Ferrous ions do not form a complex with xylenol orange under these conditions. The molar linear absorption coefficient of Fe^{3+} - XO complex is 1978 m^2mol^{-1}.

In the present system the dissolution step of benzoic acid is replaced with readily soluble sorbitol without losing dosimetric properties. Referred to as FSX (Ferrous sulphate-Sorbitol-Xylenol orange), this dosimeter is calibrated against Fricke dosimeter as reference standard.

3.2 Principle

A European patent mentions oxidation of sorbitol to glucose (Rand and Madrid 2007), which is then converted to gluconate. In this process two moles of hydrogen peroxide are generated per mole of sorbitol, as illustrated in Figure 3.1 and Figure 3.2. The reaction mentioned here takes place in the presence of enzymes. Radiation chemical oxidation of sorbitol was carried out based upon this reaction.

Since this is water based system, free radicals generated during water radiolysis. Oxidizing free radicals such as hydroxyl radicals attack organic molecules leading to their oxidation. Hydrogen peroxide generated during the process leads to oxidation of ferrous to ferric, as in Fricke dosimeter.

$H_2O \ \wedge\wedge\wedge\wedge\wedge\wedge\wedge\wedge\rightarrow e_{aq}, H^+, OH, H_2, H_2O_2$

$e_{aq} + H_3O^+ \rightarrow H^+ + H_2O$

$H^+ + O_2 \rightarrow HO^{\bullet}_2$

$Fe^{2+} + HO^{\bullet}_2 \rightarrow Fe^{3+} + HO_2^-$

$HO_2^- + H^+ \rightarrow H_2O_2$

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$

$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^-$

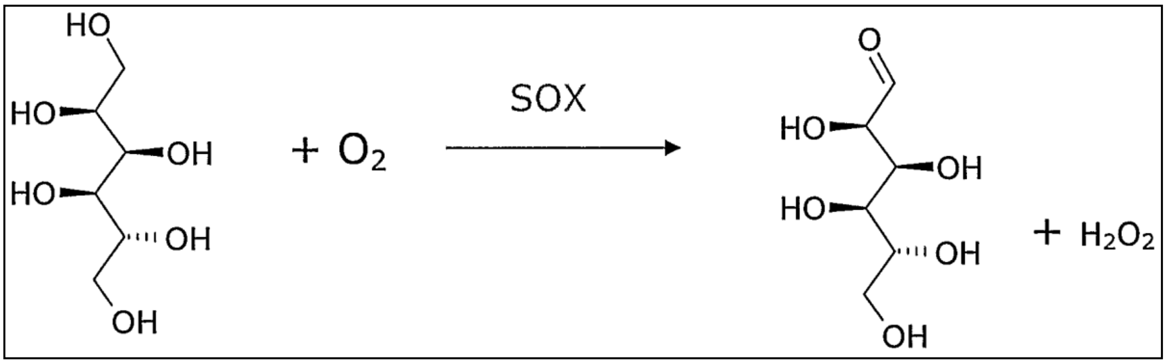


Figure 3.1: D-Sorbitol + O_2 →D-Glucose + H_2O_2

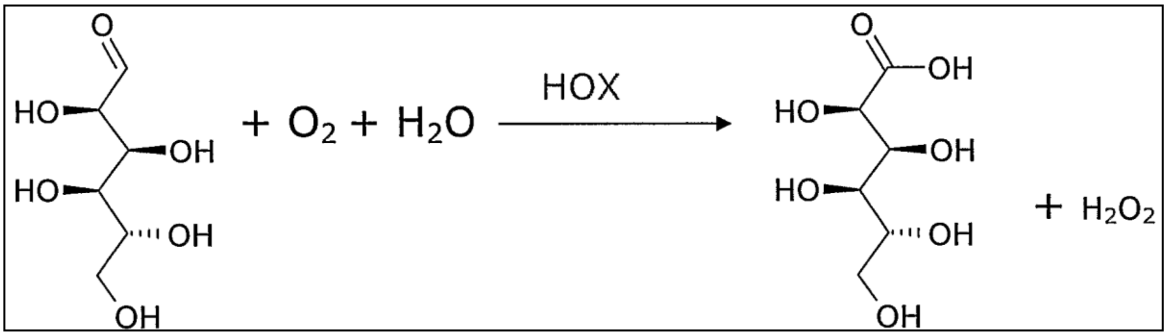


Figure 3.2: D-Glucose + O_2 → D-Gluconate + H_2O_2

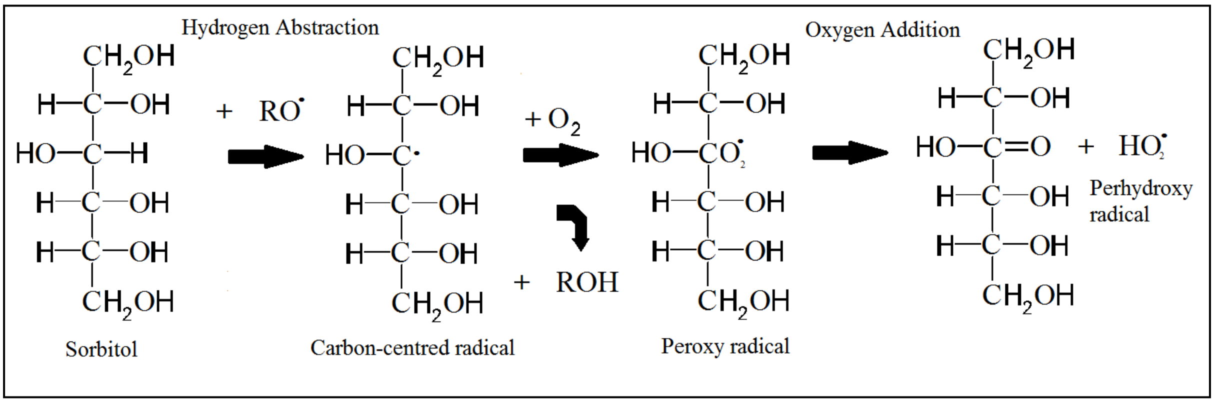


Figure 3.3: Chain propagation of Fe^{3+} oxidation enhanced by sorbitol

The chain propagation of Fe^{3+} oxidation enhanced by sorbitol is shown in Figure 3.3 (Packer and Glazer 1990). Irradiation of aqueous solution sorbitol leads to formation of oxidizing peroxy and perhydroxy radicals along with peroxides. The generated products oxidize ferrous to ferric as represented below.

$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O$ ….(1)

$R^{\bullet} + O_2 \rightarrow RO^{\bullet}_2$ ….(2)

$Fe^{2+} + RO^{\bullet}_2 + H^+ \rightarrow Fe^{3+} + ROOH$ ….(3)

$Fe^{2+} + ROOH \rightarrow Fe^{3+} + RO^{\bullet} + OH^-$ ….(4)

$Fe^{2+} + RO^{\bullet} + H^+ \rightarrow Fe^{3+} + ROH$ ….(5)

(Medium is acidic, hydronium ions are present for reactions 3 and 5 to occur)

Or

$RH + RO^{\bullet} \rightarrow R^{\bullet} + ROH$

The reactions are based on oxidation of ferrous ion by organic impurities in Fricke dosimeter

EDTA forms complexes with metals at different pH and is widely used in metal complexing titrations. Complexing agents are capable of forming chelate complexes with many cations, in which the cation is bound in a ring structure. The ring results from the formation of a salt-like bond between the cation and the carboxyl groups together with a coordinate bond through the lone pair of electrons of the nitrogen atom. If the ring is five-membered, the chelate thus formed is likely to have high stability, so the most useful chelating titrants are those that favour the formation of such rings (The International Pharmacopoeia 2014). With most metals carrying more than unit positive charge, EDTA forms highly water-soluble 1:1 complexes of such a structure that at least 3 five-membered chelate rings (Figure 3.4) (https://en.wikipedia.org/wiki/Ethylenediaminetetraacetic_acid n.d.) are formed, thus conferring high stability on the complex. In some cases, coordinate bonds other than those resulting from donation of the nitrogen lone pair of electrons may be formed with the carbonyl oxygens of the remaining carboxylic acid groups. Thus, the typical complex formed may be represented in Figure 3.5.

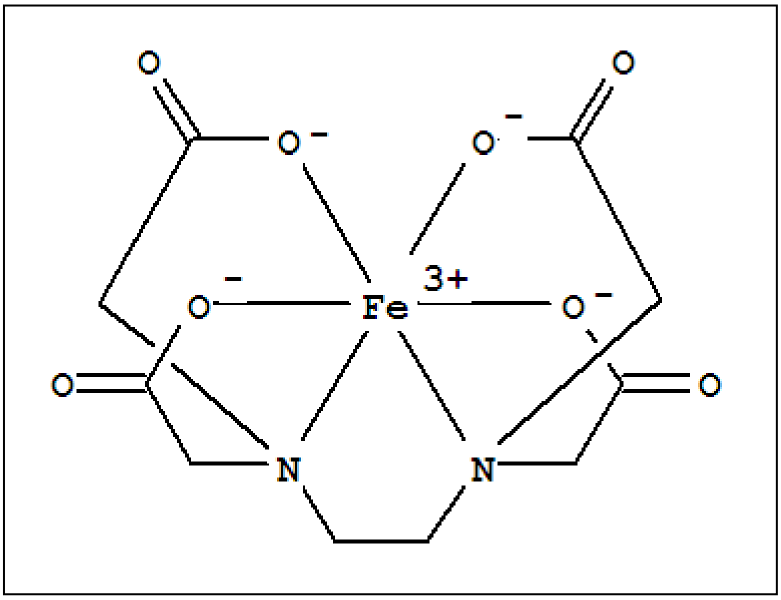


Figure 3.4: Structure of Ferric EDTA complex

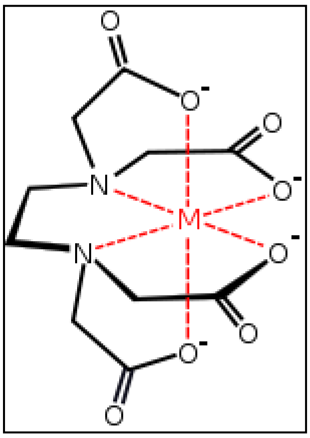


Figure 3.5: Typical complex formed by EDTA

Xylenol orange is widely used as indicator; it is conventional acid-base indicator into which iminodiacetic acid groups have been introduced thus permitting the indicator to act as a metal-complexing indicator (Figure 3.6) (www.lookchem.com n.d.). The indicator gives a clear colour change from pink-violet to yellow at the end-point in titrations of aluminium, bismuth, lead, mercury, zinc, iron (III) and may be used according to the metal being titrated.

Xylenol orange specifically complexes with ferric ion under acidic conditions [Gay and Gebicki, 1999, Gay and Collins, 1999] in 1:1 ratio, similar to that represented for EDTA.

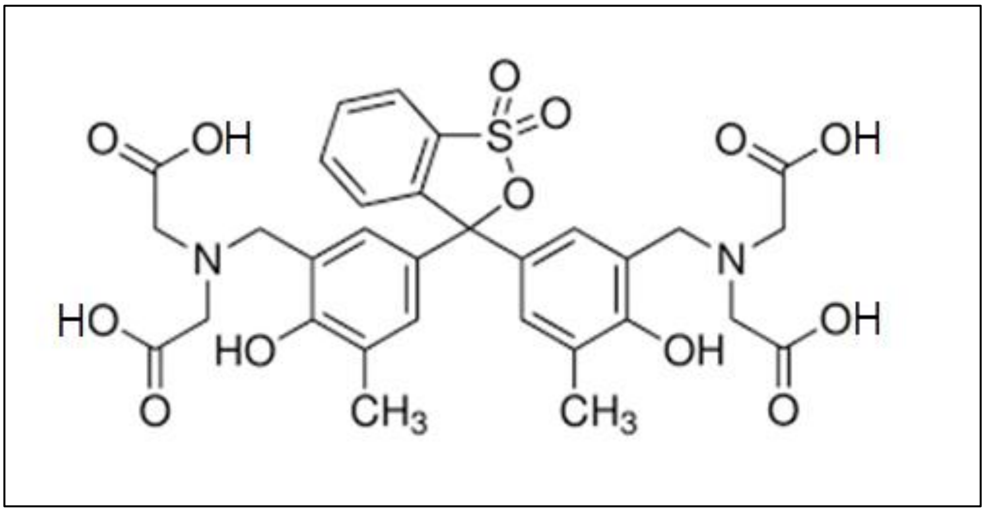


Figure 3.6: Xylenol Orange Acid Salt

3.3 Proposed structures of Ferric and Xylenol Orange complexes

Based on coordination chemistry of EDTA with metal ions and structure of ferric and metal EDTA complexes, Ferric Xylenol Orange complex structures at different pH are proposed (S. G. Mhatre, et al. 2016). Experimental conditions indicate 1:1 Ferric XO complex to be dominantly present (Figure 3.7 and Figure 3.8).

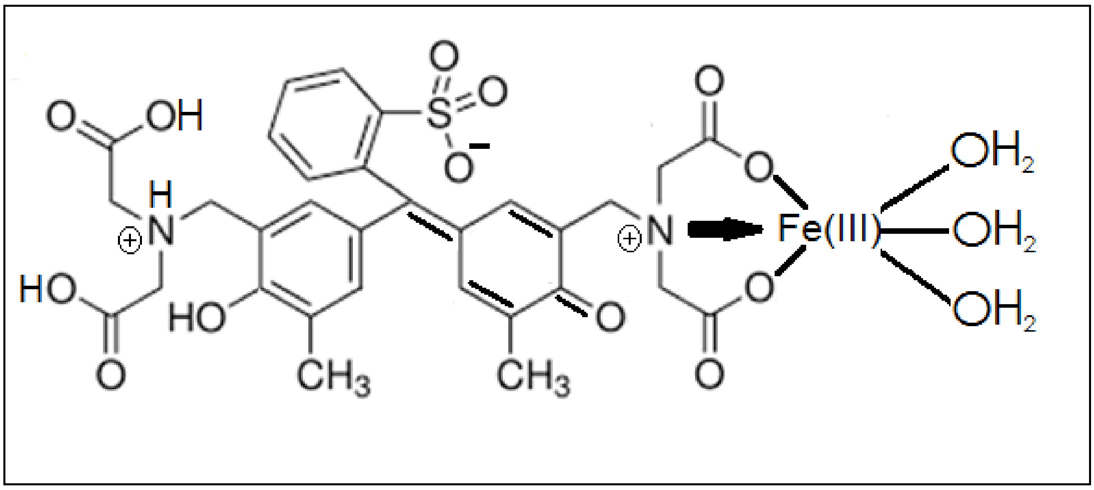


Figure 3.7: Proposed Structure of Ferric-XO (1:1) Complex at pH 2

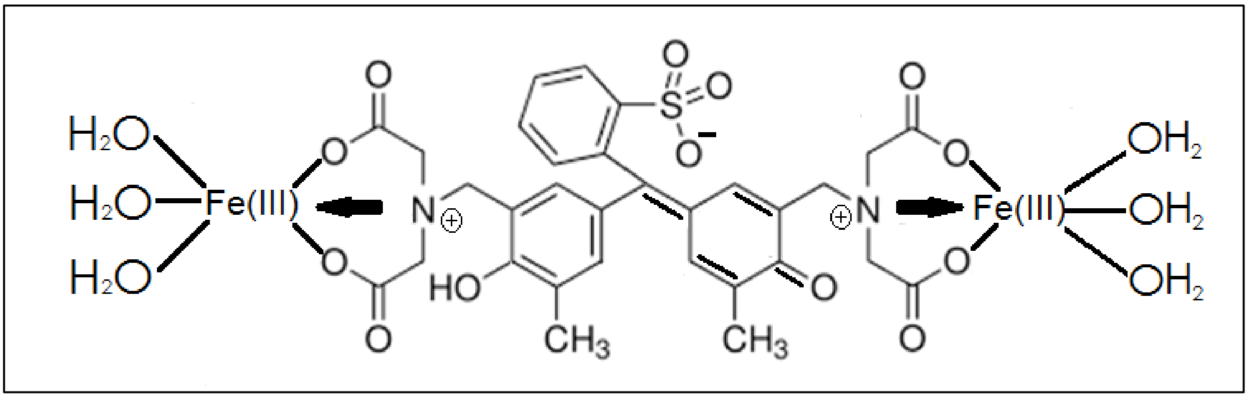


Figure 3.8: Proposed Structure of Ferric-XO (2:1) Complex at pH 5

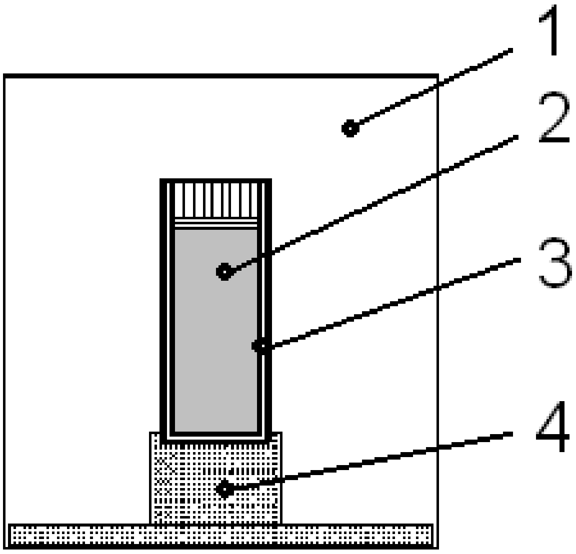
3.4 Experiment Details

3.4.1 **Reagents and Preparation**

Xylenol Orange was procured from LobaChemie, Austria. D-Sorbitol was obtained from Sisco Research Laboratories, India. Ferrous ammonium sulphate and sulphuric acid were of Analytical Reagent grade. Aqueous acidic solutions of ferrous ammonium sulphate – Sorbitol – Xylenol Orange i.e. FSX were prepared in single distilled water. All solutions were thoroughly aerated (Gupta and Nilekani 1998) by vigorously shaking the dosimetry solution, allowing air entry at regular intervals.

3.4.2 **Irradiation and measurements**

All irradiations were carried out using Co-60 gamma radiations in Gamma Chamber-220 manufactured by AECL-Canada, BI-2000, GC-900 and GC-1200 manufactured by BRIT. Polypropylene tubes were used as dosimeter containers, kept in 10 % nitric acid for 24 hours for degreasing. The degreased tubes were successively washed with normal tap water and distilled water. Dosimeter containers were preconditioned by filling them with distilled water and irradiating to dose of about 500 Gy. Jasco V 530 UV/Vis double beam spectrophotometer was used for all absorbance measurements. Dosimeter container along with the perspex build-up material provided required wall thickness *(*400 mg/cm^2*)* for attaining electronic equilibrium during irradiation (Gupta and Nilekani 1977); (Gupta, Bhat and Gomathy, et al. 1978) (Gupta, Nilekani and Madhvanath, Dependence of dose on dosimeter thickness under equilibrium conditions 1978) as shown in Figure 3.9. All dosimeter samples were irradiated at the centre position of the irradiation volume of the Gamma Chamber-900, which was initially calibrated using a Fricke dosimeter (ASTM E1026 2003).



1 → Irradiation volume of typical gamma chamber

2 → Polypropylene tube

3 → Perspex build up with 3 mm wall thickness

4→ Perspex irradiation jig

Figure 3.9: Irradiation setup

3.4.3 **Determination of optimum composition for FSX solution**

The effect of acidity has been studied in detail (Gupta and Bhat 1982), (Gupta, Bhat and Narayan, et al. 1983). FSX solutions having different concentrations of sulphuric acid were used to study acid dependence of the system. The acid concentration was varied from 10 mol/m^3 to 70 mol/m^3. Spectrum of ferric xylenol orange complex at different acid concentrations was obtained over a wavelength range of 500-600 nm measured against their respective blank solutions. Effect of acidity on absorbance at different wavelengths for the complex is shown in Figure 3.10.

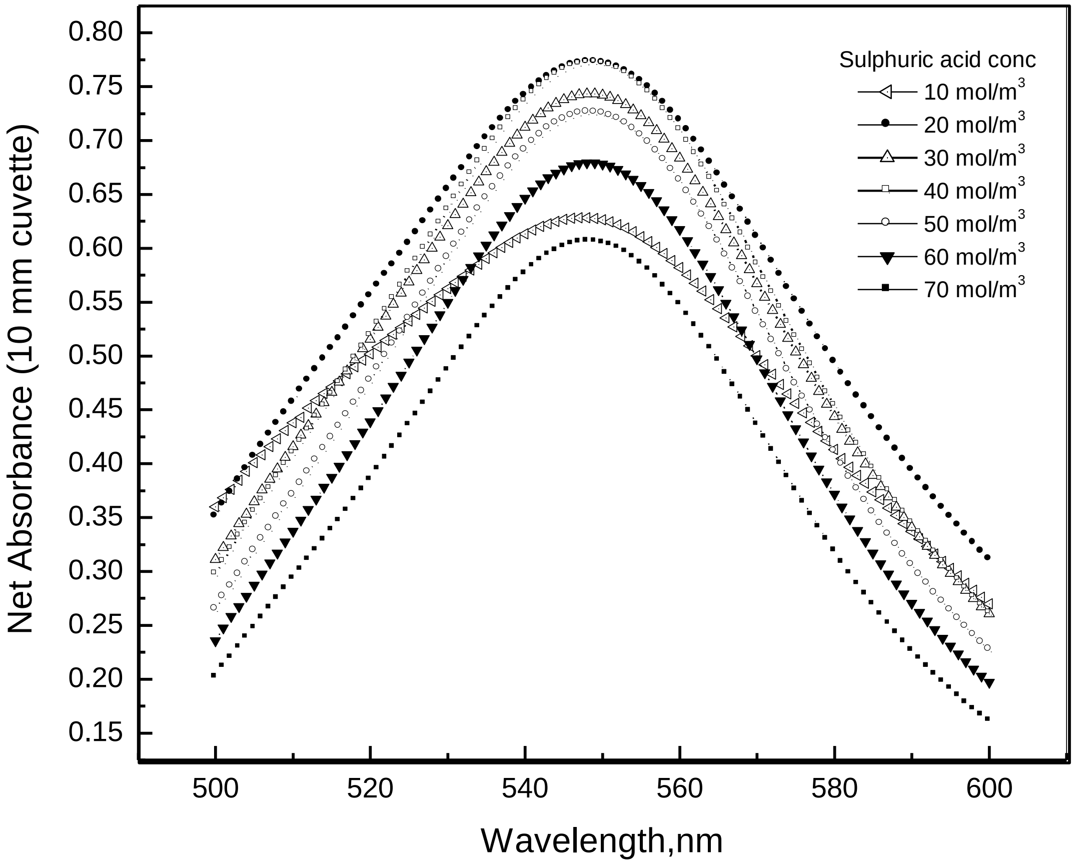


Figure 3.10: Determination of maximum absorption wavelength

All further measurements were done at 549 nm i.e. the wavelength of maximum absorption. Maximum complex formation occurs at 50 mol/m^3 sulphuric acid concentration as inferred experimentally.

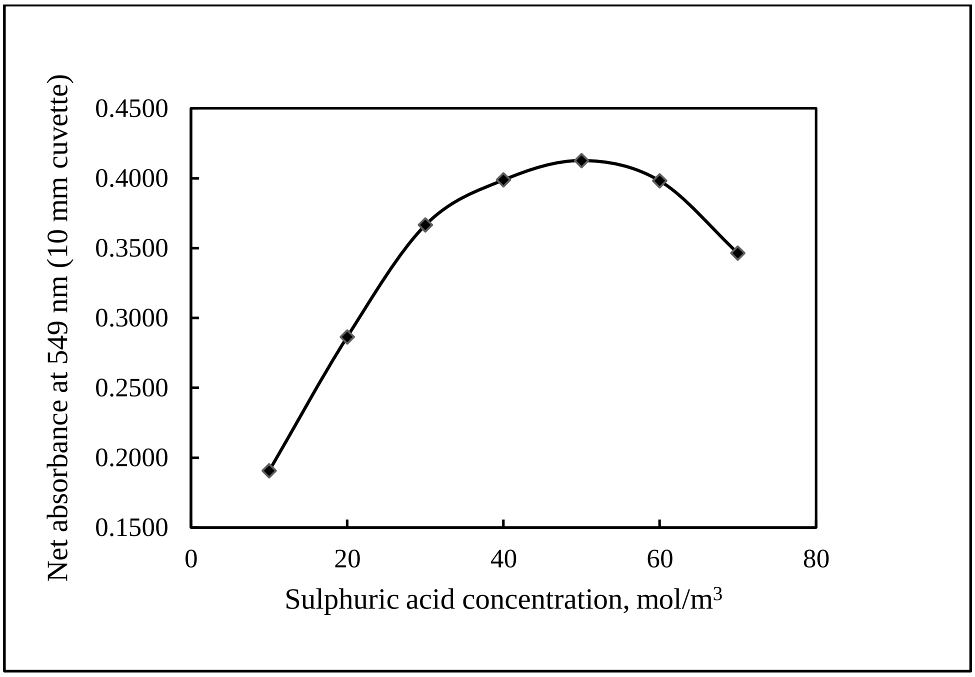


Figure 3.11: Variation of absorbance with varying sulphuric acid concentrations

Keeping concentration of other components constant i.e. 0.2 mol/m^3 ferrous ammonium sulfate and 5 mol/m^3 sorbitol, concentration of xylenol orange was optimized. The concentration of xylenol orange is optimized as lower concentration may lead to incomplete complexation of the ferric formed, leading to under estimation of dose. While higher concentration of xylenol orange will lead to increase in interaction of free radicals with xylenol orange thereby decreasing reactions with benzoic acid, thus lowering ferrous oxidation. Xylenol orange concentration was varied from 0.05 mol/m^3 to 5 mol/m^3.

3.4.4 Dose absorbance relation and trend in time

FSX filled polypropylene tubes were irradiated in GC-220; 15 dose points were chosen so as to cover the entire working range of the dosimeter i.e. 0.05 Gy to around 15 Gy, for each dose point three dosimeters were irradiated to arrive at average dose value. Based on trend observed in time dependence study, absorbance was measured after 35 minutes so as to let any slow reactions, like that of hydrogen peroxide to complete (Gupta and Nilekani 1998). The net change in absorbance values against the dose shows linear relation upto 8 Gy. The experiment was repeated thrice before representing the final dose versus absorbance relation.

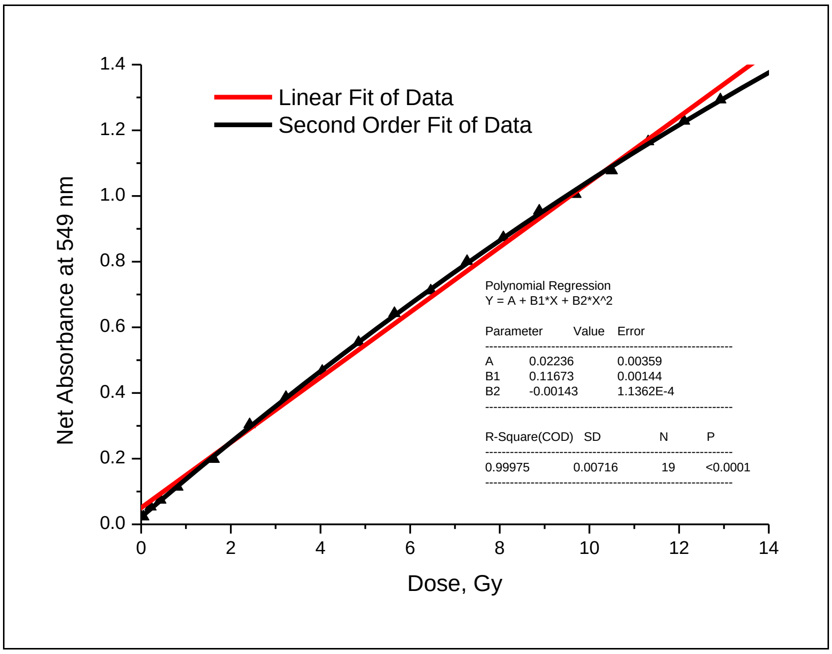


Figure 3.12: Dose-Absorbance relation (comparative)

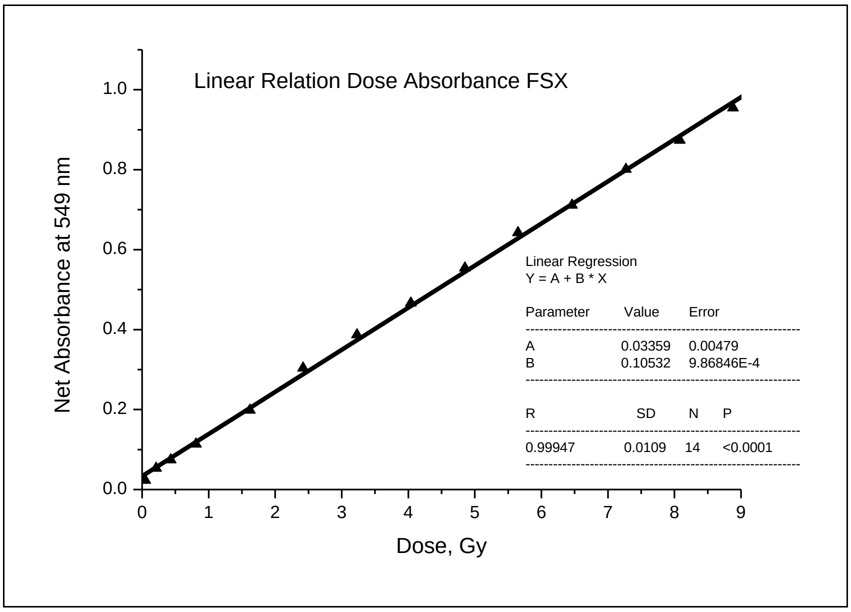


Figure 3.13: Final Dose-Absorbance relation (linear)

Two dosimeters were irradiated to 9 Gy and 12 Gy and their absorbance was recorded with respect to time at an interval of 10 minutes for determining the optimum time (range) of measurement (Shinde and Mukherjee, Dosimetric response studies of glycine FX solutions 2005). Measurements were started 5 minutes after irradiation, due to location of irradiation unit from the laboratory therefore zero time starts at 5 minutes after irradiation. Cuvette containing the irradiated solution was removed between absorbance measurements from spectrophotometer to avoid unnecessary exposure of analyzing light (Figure 3.14)

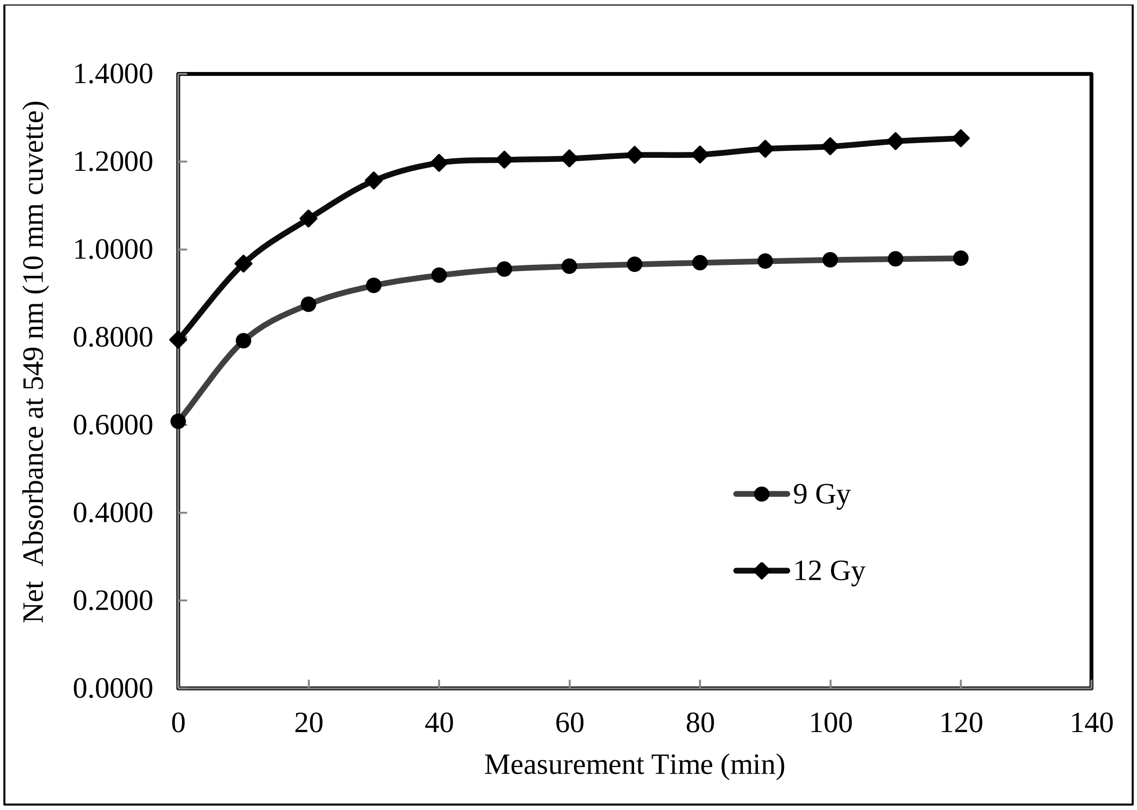


Figure 3.14: Trend with time measurement

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$ ----(1)

$Fe^{2+} + RO^{\bullet}_2 + H^+ \rightarrow Fe^{3+} + ROOH$ ----(2)

$Fe^{2+} + ROOH \rightarrow Fe^{3+} + RO^{\bullet} + OH^-$ ----(3)

$Fe^{2+} + RO^{\bullet} + H^+ \rightarrow Fe^{3+} + ROH$ ----(4)

Slow reactions (Fricke dosimeter) that are responsible for the initial rise in absorbance values

Under the experimental conditions, formation of the Ferric XO complex is completed in less than 5 min and is stable in acidic medium (Gay, J. and J.M. 1999). Hydrogen peroxide that continues to react for several minutes in the Fricke dosimeters (Sehested, Rasmussen and Fricke 1968) due to low reaction rate and thus their reaction are rate determining steps. Reactions of organic peroxides with ferrous are non-spontaneous, leading to the initial rise in absorbance value just after irradiation (Johnson and Siddiqui 1970).

3.4.5 Pre- and Post- Irradiation Stability

In pre irradiation stability study, FSX solution was irradiated to low, middle and high detectable doses and measurements were done on the day of irradiation, the exercise was repeated for next five consecutive days. Flasks containing unirradiated solution were covered with aluminium foils since light (ultraviolet and visible) have been found to increase the ferrous ion oxidation (Gupta and Nilekani 1998). The unirradiated solutions were stored at room temperature under normal laboratory conditions. Each reading taken is an average of three absorbance measurements.

On the tenth day, the optical density of the unirradiated solution was found to very high; irradiation was not carried out since the net optical density would be too low for any dose inference. Table 3.1 represents the results of this exercise. The pre irradiation stability exercise was repeated using unirradiated solution refrigerated to temperatures in the range of 5-10 °C. All refrigerated solutions were allowed to attain room temperature, following which they were irradiated as done in the previous exercise. Due to the observed stability of the unirradiated solution, the exercise was repeated on the fifth, tenth, fifteenth and finally on thirtieth day after the solution was prepared. Results of the exercise are tabulated in Table 3.2.

Table 3.1: Pre-irradiation stability of FSX (unrefrigerated)

Dose Storage time	Control	1.58 Gy	6.30 Gy	12.60 Gy
Day 0	0.3943	0.1918	0.6901	1.2775
Day 1	0.3964	0.1914	0.6901	1.2807
Day 2	0.4197	0.1892	0.6676	1.2602
Day 4	0.4748	0.1940	0.7082	1.2611
Day 5	0.4785	0.1825	0.6875	1.2771
Day10	0.5607	0.1579	0.1913	0.6310

Table 3.2: Pre-irradiation stability of FSX (refrigerated)

Dose Storage time	Control	1.75 Gy	3.51Gy	7.01Gy
Day 0	0.3619	0.3719	0.4238	0.7627
Day 5	0.3667	0.3765	0.4265	0.7645
Day 10	0.3712	0.3778	0.4315	0.7665
Day 15	0.3722	0.3864	0.4322	0.7781
Day 30	0.3820	0.4216	0.5412	0.9103

The high absorbance of unirradiated solution is due to the ferric present in the solution generated thermally by ferrous oxidation in presence of dissolved oxygen (Morgan and Lahav 2007) combining with xylenol orange to form Fe^{3+} - XO complex. As the molar linear absorption coefficient of Fe^{3+} - XO complex is high, 1978 m^2mol^{-1}, the unirradiated control absorbance values are high. For post irradiation stability study, ten FSX solution samples were irradiated to same dose. The exercise was repeated for two more dose values in order to cover the entire dose range of the dosimeter. Single set of dosimeters (same dose value) were irradiated for same time on the same day to reduce error due to dose rate effect and radioactive decay correction. One sample from each set of dose was analysed for its optical density, starting from day of irradiation up to fifth day, as after fifth day the absorbance values varied beyond scope of analytical interest. The absorbance values keep on increasing steadily suggesting a group of slow reactions occurring in the medium, similar to that observed in FBX (Gupta and Narayan 1974), all dosimeters were stored covered in aluminum foils at room temperature under normal conditions during all measurements. Table 3.3 gives the results of the study for post-irradiation stability of FSX.

Table 3.3: Post-irradiation stability of FSX

Dose Storage time	Control	0.51 Gy	6.08 Gy	12.16 Gy
Day 0	0.3962	0.0799	0.6704	1.2377
Day 1	0.4061	0.4949	1.1201	1.7347
Day 2	0.4553	0.5065	1.1038	1.7265
Day 3	0.4719	0.5244	1.1279	1.7439
Day 5	0.4954	0.5596	1.1653	1.7727

3.4.6 **Reproducibility Study**

Reproducibility is one of the most important factors for any system to establish as a dosimeter. For reproducibility study, ten tubes filled with FSX solution were irradiated to same dose (same irradiation time on the same day) and optical densities of these solutions were measured on the day of irradiation. The exercise was repeated for five different doses. The entire study was repeated twice for testing statistical variation. Table 3.4 represents the reproducibility of the system.

Table 3.4: Dose response reproducibility study

Dose, Gy	Net Absorbance Average	Standard Deviation	Coefficient of variation (%)
0.047	0.0244	0.0019	0.78
2.94	0.3494	0.0014	0.40
4.90	0.5549	0.0029	0.52
6.30	0.6983	0.0064	0.91
9.66	1.0071	0.0081	0.81

3.5 Results and Discussions

The optimum composition of FSX solution for use as low level dosimeter was established. Figure 3.10 highlights the effect of acidity on absorbance at different wavelengths and the maximum complex formation occurs at 50 mol/m^3 sulphuric acid concentration. The wavelengthof maximum absorption of Ferric - XO complex was found to be at 549 nm. Figure 3.15, Figure 3.16, and Figure 3.17show the effect of xylenol orange, sorbitol and ferrous ion concentrations respectively on absorbance and the maximum net absorbance is obtained for XO concentration of 0.5 mol/m^3, 10 mol/m^3 sorbitol concentration and ferrous ion concentration of 0.2 mol/m^3.

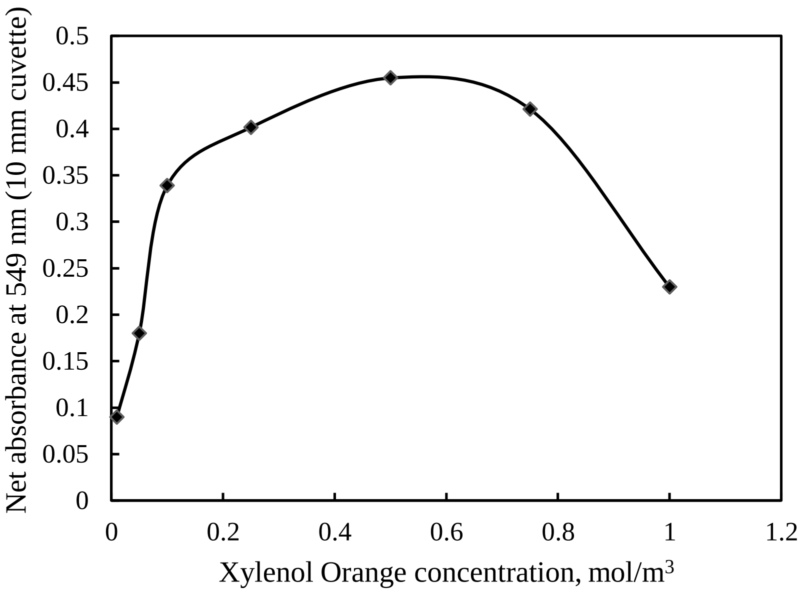


Figure 3.15: Optimum Xylenol Orange concentration

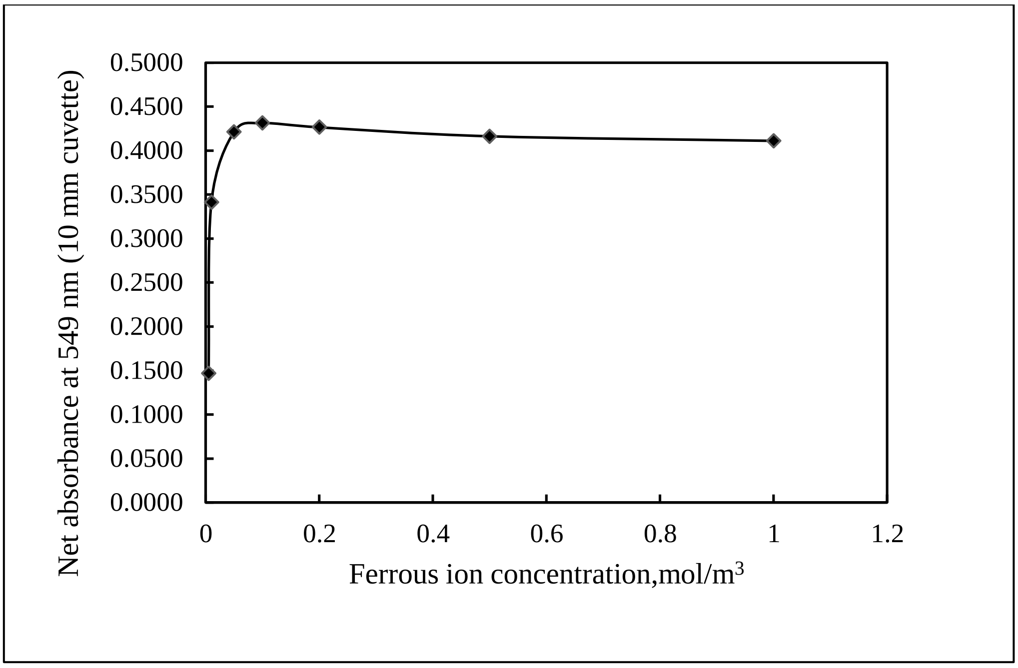


Figure 3.16: Optimum ferrous ion concentration

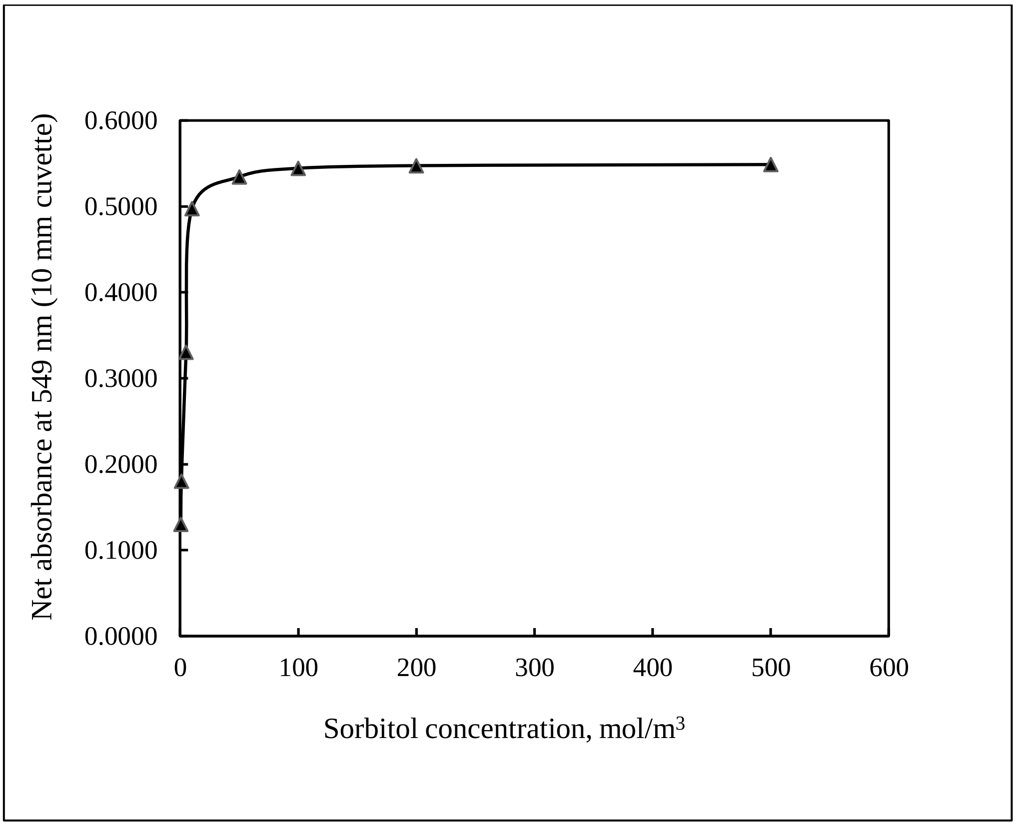


Figure 3.17: Optimum sorbitol concentration

It is clear from trend in time measurements, that all absorbance measurements must be performed at least 35 minutes after the irradiation; it is also advisable to complete the measurements within 120 minutes, to minimize the error due to variation in absorbance with time.

Figure 3.12 and Figure 3.13show the plot of net absorbance values versus dose indicating the upper and lower limit of the dosimeter to measure gamma radiation i.e. from 0.05 Gy to 12 Gy. The dose response curve is non-linear with second order polynomial fit. Less than 1% coefficient of variation observed during dose reproducibility studies suggests its application in measuring low doses with high accuracy. It is observed during earlier studies (Gupta and Jain 1994) that the brand and origin of the chemicals used for dosimeter preparation may alter the dose response and other likewise factors therefore it is advisable to establish these beforehand to avoid erroneous results.

Table 3.1 and Table 3.2 show the pre-irradiation effect of FSX under unrefrigerated and refrigerated conditions respectively. Table 3.3 shows the post-irradiation effect of FSX. The study suggests that the unirradiated solution, stored in dark environment under refrigerated conditions in the temperature range of 5-10 °C can be used up to one month for dose evaluation. However, irradiated solutions must be evaluated on the day irradiations are carried out so as to minimize error due to post-irradiation effect.

3.6 Conclusions

The study suggests that sorbitol can be used as a radiolytic sensitizer in Ferrous Xylenol Orange based system for measuring low doses with high reproducibility. Being a liquid dosimeter it can be used for dosimetry of complex shapes and geometries. Using FSX, low dose irradiation units such as blood irradiators and gamma chambers can be standardized. Being highly reproducible it can be used for calibration of low activity sources, using Fricke dosimeter used as reference.

Sorbitol is highly water soluble and commonly available as sweetener. The FSX dosimeter developed is simple to prepare and use and can be stored for more than six months when kept under refrigerated conditions (Mhatre and Adhikari 2012).

Chapter 4 Development of New Radiation Indicator and Radiochromic Dosimeter System

4.1 Introduction

Visible colour change caused by ionizing radiation is termed as radiochromism. Radiochromic phenomenon can be applied to radiation processing industry in several ways. In radiation indicators, colour change associated with irradiation is related to dose, thus validating the process. Advantage of radiochromic dosimeter systems is the visible colour change associated with them. Many systems are developed worldwide over the years. Commercially available and most widely used radiochromic dosimeters are leuco dye based patented systems that are very expensive. A leuco dye is a dye whose molecules can acquire two forms, one of which is colorless and can be reverted back to the original dye. Common principle involved is radiolysis of leucodyes to reform the original coloured dye. Alternatively leuco dyes are oxidised using oxidising agents to form the original dye. The amount of dye formed is proportional to the dose received.

Aqueous solutions of formyl violet cyanide (FV-CN) have been investigated for potential use in radiation dosimetry using both absorption and fluorescence evaluation (Ebraheem, et al. 2007); (Rativanicha, et al. 1977). The high solubility of 2,3,5-triphenyl-tetrazolium chloride (TTC) in alcohols has been utilised for developing a liquid dosimeter and shows a linear response of increase in absorbance with dose over the range 1-16 kGy (Kovacs, et al. 1995). The Spectrophotometric sensitivity of chromophoric chemical dosimeters can be enhanced by increasing the optical path length through the light absorbing medium. This approach is used with optical waveguide (OWG) dosimeters, consisting of liquid-phase light-propagating media filling the core of long, thin flexible polymer tubing (Radak, Mclaughlin and Simic 1986). Recently, nitro blue tetrazolium (NBT) solution dosimeters based on radiation-induced reduction of NBT^{2+} have been developed [(Rabaeh, Moussa and Basfa 2013)].

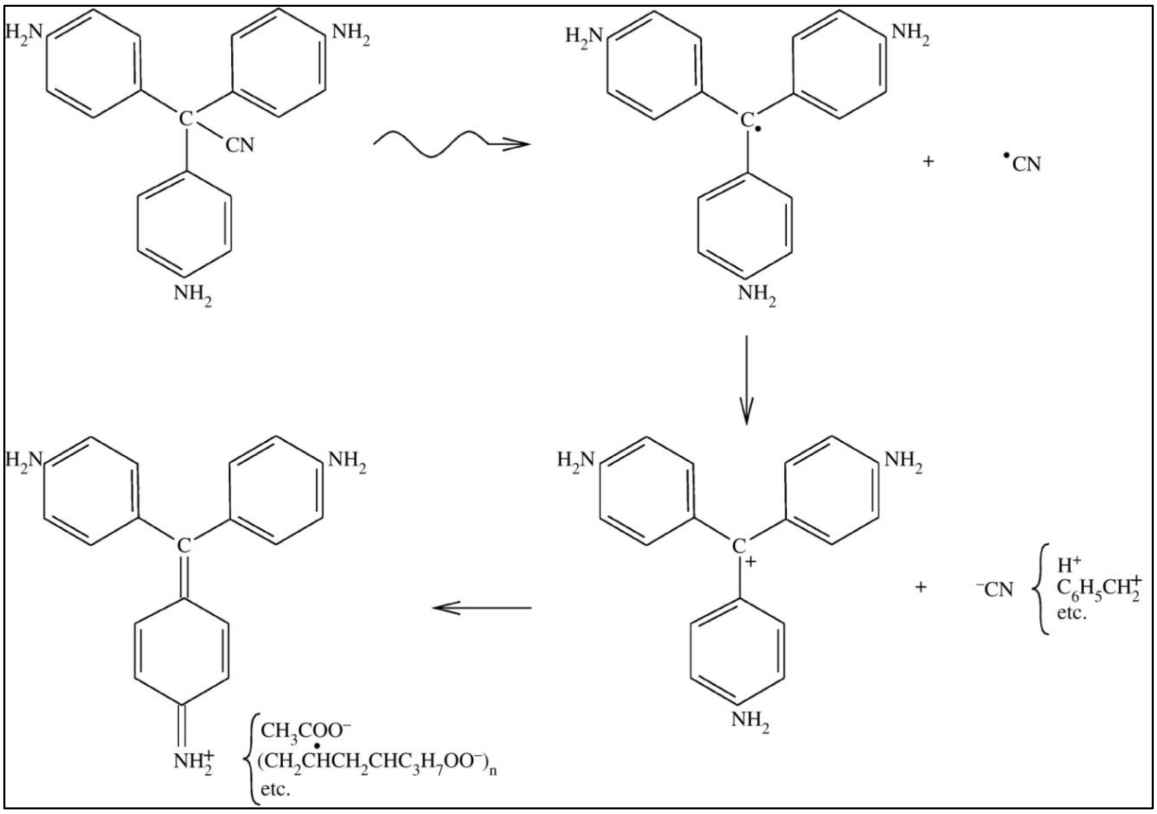


Figure 4.1: Radiation-chemical reaction scheme for the radiochromic change of pararosaniline leuco-cyanide to the dye.

Imported systems available in India are patented and very expensive (each dosimeter can cost between Rupees 350-450 that excludes the cost of analytical instrument and its maintenance). Development of indigenous system is need of the day as no indigenous system is commercially available. Moreover, most of these systems use cyanide for leuco dye synthesis that is dangerous for environment and life. With this as background, a new system was tested for use as radiation indicator and further tests were performed to suggest its use as a radiochromic dosimeter.

Work started with search for reactions leading to contrasting change in colour with the feasibility to display radiochromism. Few systems were selected, the reaction feasibility was tested. It was observed that the commercially available systems like Riso B3 radiochromic dosimeter films were developed on the basis of photochemical conversion of pararosanilne cyanide to its dye precursor. The leuco dye pararosaniline cyanide is radiolysed to pararosaniline by UV light (McLaughlin 1966) (Figure 4.1). Its application as radiochromic dosimeter was successfully tested and is available worldwide for widespread use in dosimetry applications.

Also radiation plays the role of activation for reactions that are energetically not possible under normal laboratory conditions. Unlike photochemistry, radiation chemistry is highly nonspecific and some unexpected reactions are highly expected. Many systems were tried and based on the preliminary results a few were selected for further study.

Two types of systems are discussed, first based on Schiff's test of leuco pararosaniline and the second based on radiochemical halogenation. The journey from reaction feasibility to dosimetry is discussed in detailed.

4.2 Leuco dye - based liquid radiation indicator

Present chapter discusses development of radiation processing system which is based on Schiff's test of leuco pararosaniline.

4.2.1 Principle

Fuchsin solutions appear coloured due to the visible wavelength absorbance of its central quinoid structureviologenthat are "decolorized" upon sulfonation of the dye at its central carbon atom by sulfurous acid or its conjugate base, bisulfate (Figure 4.2). This reaction disrupts the otherwise favored delocalized extended pi-electron system and resonance in the parent molecule. The further reaction of the Schiff's reagent with aldehydes is complex.Several research groups have reported multiple reaction products with model compounds. In the currently accepted mechanism, pararosaniline and bisulfite combine to yield the "decolorized" adduct with sulfonation at the central carbon. The free, uncharged aromatic amine groups thereafter react with the aldehyde being tested to form two aldimine groups. These groups have also been named on the discoverer as Schiff bases (azomethines), with the usual carbinolamine (hemiaminal) intermediate being formed and dehydrated en route to the Schiff base. These electrophilic aldimine groups then react with further bisulfite, and the Ar-NH-CH(R)-SO_3–product (and other resonance-stabilized species in equilibrium with the product) gives rise to the magenta color of a positive test (Li and Zhao 2006).

Primary alcohols such as ethanol, are oxidized to aldehydes (Antoniadou 2012) photocatalytically (UV) (Figure 4.3), experiments were carried out to check radiocatalytic (high energy) feasibility of the reaction. Ethanol, ethylene glycol, ethyl acetate, glycerine were tested for feasibility in the above reaction mechanism (Figure 4.4). Solution of Schiff’s reagent (pararosaniline-sulphite) and glycerol/ethanol, in acidic medium, when irradiated, displayed promising results. The un-irradiated solution is colourless and develops magenta colour upon irradiation.

Pararosaniline (Fuchsin) is converted to leuco fuchsin upon treatment with sodium sulphite or sulphur dioxide. The loss of the quinoid ring of pararosaniline, by the change from double to single bonds because of the addition of -SO_3H, results in the formation of Schiff's reagent or fuchsin-sulphurous acid.

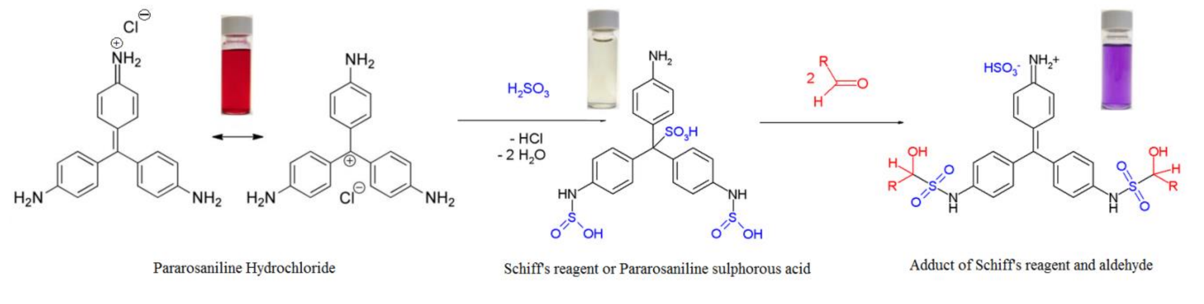


Figure 4.2: Postulated reaction mechanism of Schiff’s reagent-based aldehyde detection technique with changes in colour

Aldehyde converts the decolourised fuchsin to coloured complex or adduct. The single bonds of Schiff's reagent, reform into a quinoid ring due to the addition of aldehyde leading to the formation of contrastingly coloured adduct.

Primary alcohols are oxidized to their respective aldehyde upon irradiation in presence of mineral acids to their respective aldehydes for e.g. ethanol is oxidized to acetaldehyde by radiolysis (Freeman 1974). Transition metal ions and some anionic species were found to catalyse oxidation of alcohols (Maignien, Aït-Mohand and Muzart 1996). (Clark and Macquarrie 2002); (Velusamy and Punniyamurthy 2004).

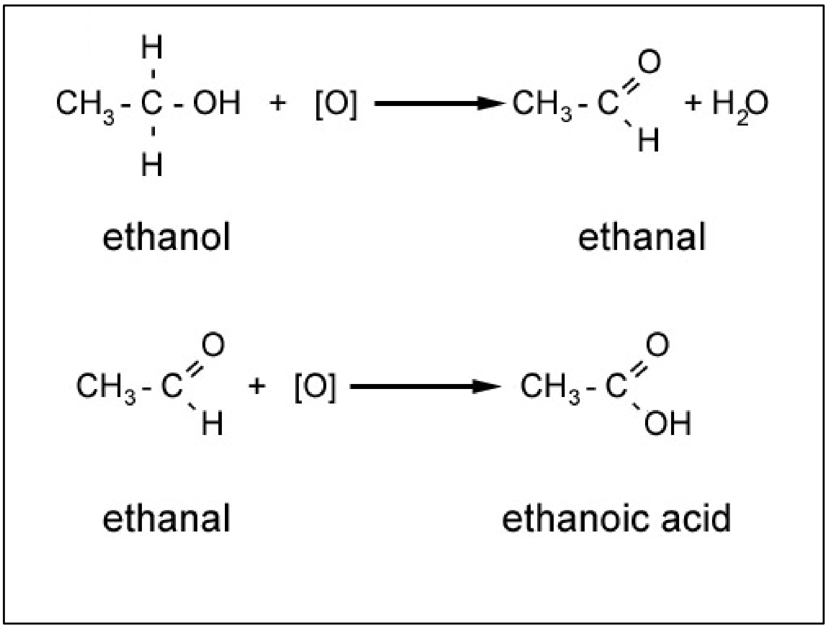


Figure 4.3: Scheme showing chemical oxidation of ethanol

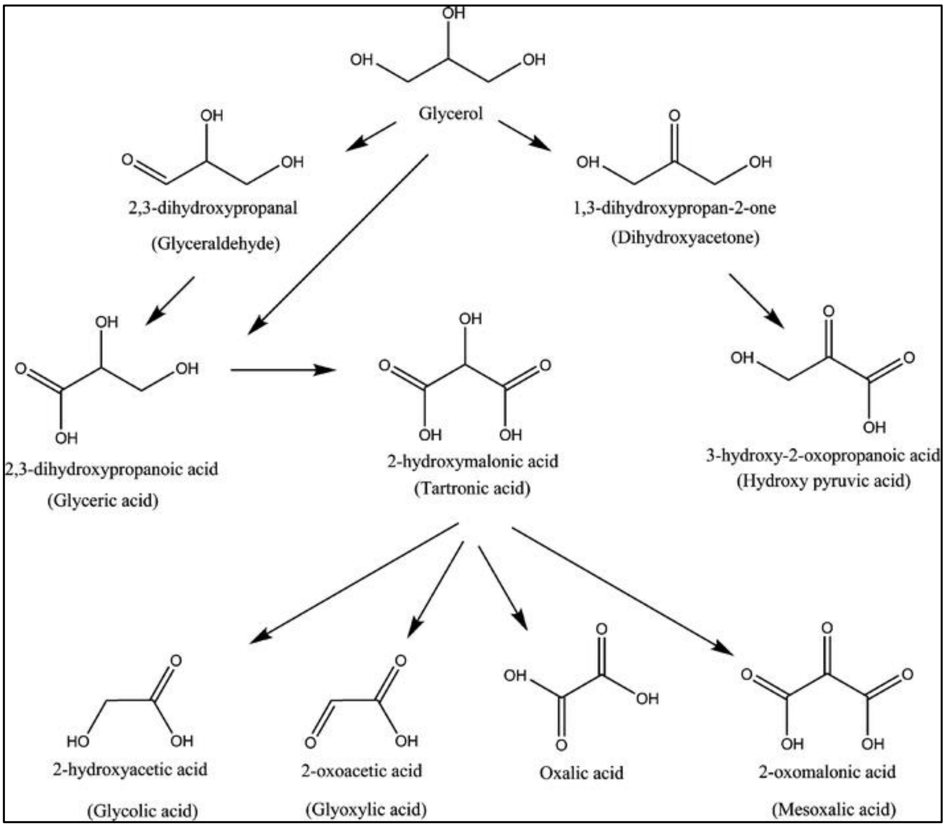


Figure 4.4: Scheme showing chemical oxidation of glycerol

4.2.2 Possible reaction mechanism for Schiff's reagent-based system

Figure 4.5 and Figure 4.6 show the possible reaction mechanism for oxidation of ethanol and glycerol respectively. Figure 4.7 gives the adduct formation of the aldehyde (formed radiolytically) with Schiff's reagent. (Antoniadou 2012)

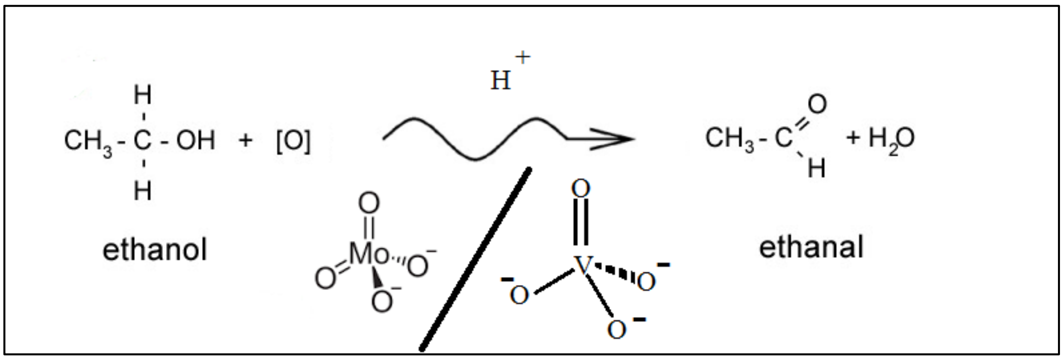


Figure 4.5: Radiolytic oxidation of Ethanol

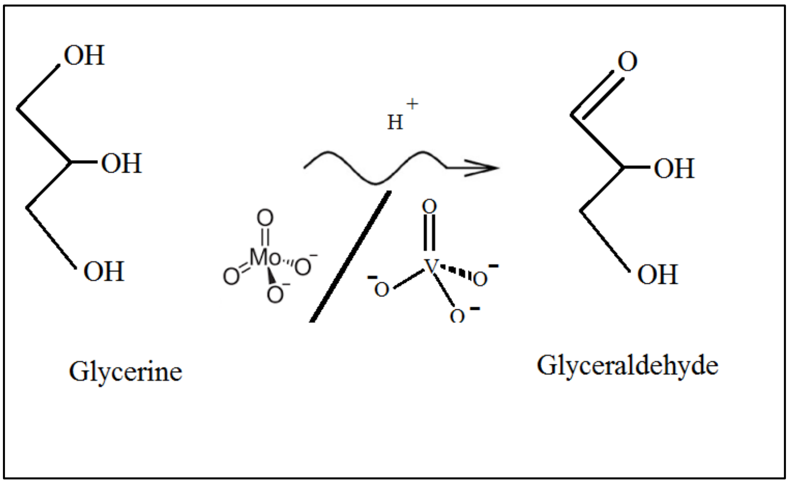


Figure 4.6: Radiolytic oxidation of Glycerine

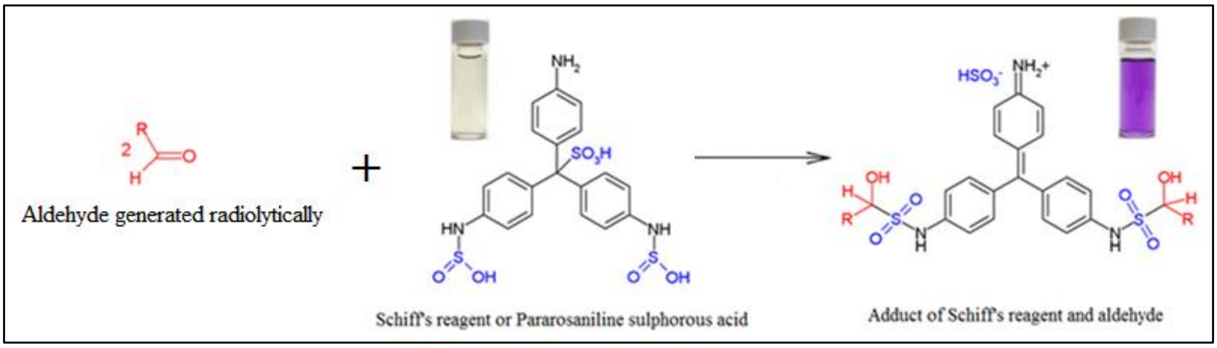


Figure 4.7: Aldehyde forming adduct with Schiff’s reagent

4.2.3 **Experiment Details**

Initially distilled water solutions of ethanol (10 %) along with sulphuric acid (50mol/m^3) were irradiated by gamma radiation and tested for the formation of aldehydes. Concentration of ethanol was varied between 5-15 %. Schiff’s reagent was prepared by adding 0.05 mol/m^3 sodium sulphite in 10 mol/m^3 pararosaniline solution. Schiff’s reagent was added to irradiated solution to test formation of aldehydes. This experiment was done to check the aldehyde formation in absence of catalyst and to assess degree of autocatalytic oxidation of alcohol in the presence of sulphuric acid. In the next set of experiments, solution of ethanol and sulphuric acid (proportions and concentrations of ethanol and sulphuric acid used were same as in earlier experiment) were irradiated by gamma radiations with molybdenum added (as ammonium molybdate 5 mol/m^3) as catalyst. pH of the solution was varied using sulphuric acid and sodium hydroxide so as to cover the entire pH range. The reaction was found to be optimum at low pH (around 5). The experiments were repeated for vanadium (added as ammonium vanadate 5 mol/m^3). Aldehydes are produced during radiolysis of ethanol as observed visually by performing Schiffs test. On the basis of the above experiments, glycerine, polyvinyl alcohol and ethyl acetate were used and similar set of experiments were carried out. Polyvinyl alcohol was chosen in this study as it can be used for casting films. The objective of experiments was to test the feasibility of the reaction and finalising reagents. Experiments were also performed using hydrochloric acid, however sulphuric acid seemed to be better alternative as the solutions prepared using it were colourless. Solutions were prepared from ethanol, glycerine and polyvinyl alcohol (5 mol/m^3 in 50mol/m^3 sulphuric acid each) and Schiff's reagent along with transition ion catalyst.

4.2.3.1 **Reagents and Preparation**

Pararosanile HCl dye was used for preparation of Schiff's reagent. Ethanol glycerine and polyvinyl alcohol were used as alcohol group containing compounds. Sodium sulphite was used for converting the pararosaniline dye to its colourless form.

4.2.3.2 **Irradiation and Measurement**

All irradiations were carried out in gamma chamber GC-900 and GC-1200. Spectrophotometric measurements were done using spectrophotometer for liquid samples.

4.2.3.3 **Pre- and Post- Irradiation Stability**

All samples were stored in dark at room temperature to study pre and post irradiation stability.

4.2.4 **Results and Discussions**

Initial experiments suggested, aldehydes were produced during irradiation of alcohol solutions as positive results were obtained with Schiff's test. The reason for choosing the ethanol and glycerine is their ease to form aldehydes upon oxidation; secondary alcohols form ketones while tertiary alcohols are difficult to oxidize. On irradiation of alcohols with molybdenum and vanadium catalysts, the aldehyde formation was enhanced to a great level. In acidic medium, molybdenum and vanadium ions oxidise alcohol groups in ethanol, glycerine and polyvinyl alcohol to their respective aldehydes with the help of water radiolysis products. A solution containing alcohol and molybdenum in acidic medium along with Schiff's reagent was tested for use as a radiochromic dosimeter. Absorption spectra of the irradiated solutions were recorded and are shown in Figure 4.8. However, the system after irradiation is quite unstable as the colour formed reverts back within a short time period as in case of solid system or the adduct formed getting precipitated on container walls in case of liquid system.

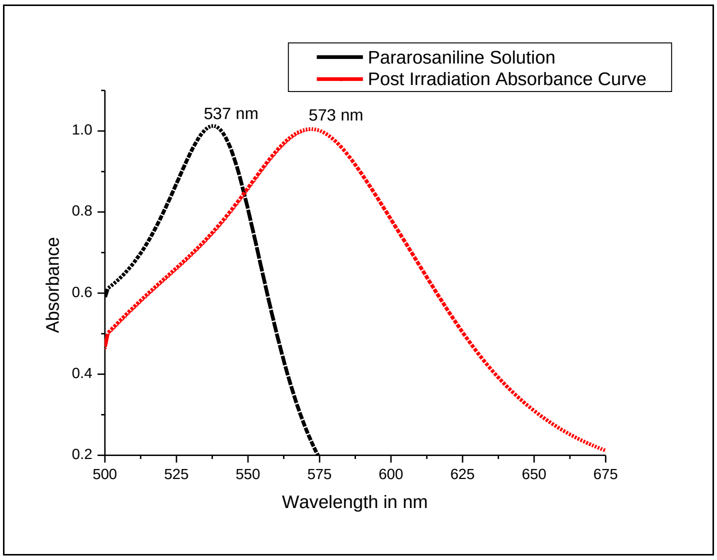


Figure 4.8: Spectra of pararosaniline solution containing ethanol and sulphuric acid in comparison with spectrum of irradiated solution

It was found that solution after irradiation tends to adhere to the walls of the containment vessel. The adduct formed adheres the walls of container permanently in case of polymer and glass vessel. Results of the experiments are shown in Table 4.1.

Table 4.1: Irradiation experiments in solution form with Schiff's reagent

Additve along with Schiff's reagent	**Molybdate catalyst (5 mol/m^3)**	**Vanadate catalyst (5 mol/m^3)**
	Colour observed after irradiation	
Glycerine (5%)	Magenta	Magenta
Ethanol (5%)	Dark magenta	Dark magenta
Polyvinyl alcohol (5%)	Magenta changing to pink(reversible)	Magenta changing to pink (reversible)

Polyvinyl alcohol films of the solution were cast and irradiated upon drying as it was difficult to measure absorbance of the solutions due to adduct adhering to the cuvette walls. The results of the exercise are shown in Table 4.2. In liquid and solid medium, reversible colour change can be attributable to the reaction of Schiff's reagent with unattached aldehydes. The aldehydes react with Schiff's reagent to produce a deep pink background.

Table 4.2: Experiments in Polyvinyl alcoholfilm

Additve along with Schiff's reagent	**Molybdate catalyst (5 mol/m^3)**	**Vanadate catalyst (5 mol/m^3)**
	Colour observed after irradiation	
Glycerine (5%)	Light Magenta (unstable)	Magenta (unstable)
Ethanol (5%)	Dark Pink (unstable)	Dark Pink (unstable)
Ethyl Acetate (5%)	Magenta changing to pink (reversible)	Magenta changing to pink (reversible)

4.2.5 **Conclusions**

The study suggests that the pararosaniline based system is quite unstable with respect to absorbance both in liquid and polyvinyl alcohol film form. In liquid form, post irradiation product formed tends to adhere walls of irradiation container, while in the film form the adduct formed is unstable, reverting back to its original form within short time. Increasing the sulphite concentration results in increase of threshold response of the system to great degree but there was no improvement in the stability observed for film based system.

Water soluble polymers without alcohol group scan be tried so as to minimize the reversal of the developed colour as the unreacted alcoholic groups may be responsible for reversal of the reaction.

4.3 Iodine - based liquid indicator for radiation processing

As part of development of radiation indicator, a new method for eythrosine synthesis was studied. The reason for choosing the reaction was due to the contrasting colour difference of reactant fluorescein (fluorescent yellow) dye from the final product erythrosine (dark red) formed (Feigl and Anger 1972). To function as radiation processing indicator, a contrasting colour change should be produced after receiving required radiation dose. Erythrosine (2-(6-Hydroxy-2,4,5,7-tetraiodo-3-oxo-xanthen-9-yl) benzoic acid) is a derivative of fluorescein. It is used as food coloring agent, printing inks, biological stain, radio opaque mediums, and sensitizer for orthochromatic photographic films. Present work discusses the formation of erythrosine through radiation chemical pathway. In radiation processing industry, this can be used for indicating the dose received by a commodity when processed by radiation. The indicator serves as a go no-go type indication for radiation processing applications. Additionally, radiation indicators can be used to ascertain the amount of fixed dose received by a commodity for e.g. in sterilization of medical products.

4.3.1 **Principle**

Iodination of fluorescein is carried out in several ways. Elemental iodine is heated with fluorescein and bicarbonate, the fluorescein is iodinated in steps to form erythrosine. In electrochemical technique of erythrosine synthesis, electric current is passed through a solution of sodium carbonate containing iodine and fluorescein at a divided cell (Jagannathan and Anantharaman 1987). Electrochemical technique describes erythrosine synthesis using different electrolyte solutions with varying anode material and varying current densities (Vasudevan and Ananthraman 1994). A patented method describes formation of halogenated fluorescein with varying degrees of iodination using iodide salt with oxidizers and fluorescein disodium salt with the help of heat (Volpe 2006) (Maria Volpe 2008). A new technique for erythrosine synthesis by iodination of fluorescein is discussed here. Radiation chemical synthesis of erythrosine was developed using ionizing radiation and the reactions were enhanced using catalysts. The developed process avoids use of toxic elemental iodine and is based on electrophilic halogenations by free radicals generated from water radiolysis, thus can be scaled up for commercial manufacture of the dye without any catalyst. The developed technique is a new and untested method for erythrosine synthesis using radiation technology.

In electrophililc halogenation, iodine is generated thermally. Iodine can also be generated by reaction between iodide and iodate in acidic medium (Xie, Michael and Margerum 1999).

$$IO_3^- + 5\,I^- + 6\,H^+ \longrightarrow 3\,I_2 + 3H_2O$$

In acidic medium above reaction would take place leading to iodine formation. However the presence of fluorescein in the solution form requires a fairly high pH to prevent precipitation.

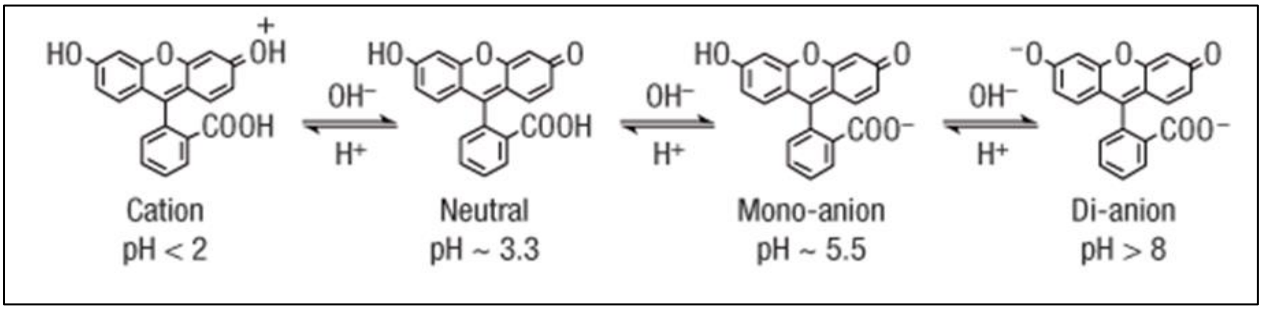


Figure 4.9: Different tautomeric forms of fluorescein

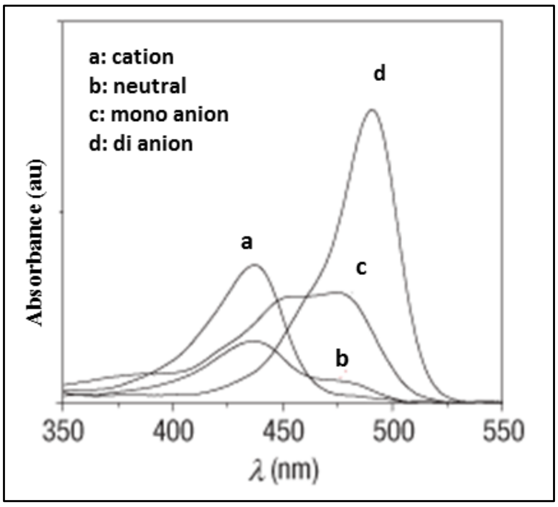


Figure 4.10: Absorption spectra of different tautomeric forms of fluorescein

Fluorescein exists in different tautomeric forms at different pH values as shown in Figure 4.9 and Figure 4.10. The phenoxide formation at alkaline pH facilitates iodination, as the adjacent carbon atom becomes an electron rich centre.

Higher pH favours the fluorescein dissociation, leading to increase in iodination due to phenoxide ion formation however at higher pH the reactivity of iodine is reduced. Thus, a balance of pH with right choice of reactants is needed to optimize this reaction.

Iodine can be generated by irradiating iodide solutions. In iodide-iodate dosimeter (Rahn 2003) triiodide is formed upon exposure to ionizing radiation. The exact reaction mechanism is unknown, however free radicals and other reactive species generated by water radiolysis are found to initiate the reaction. The triiodide formed is in equilibrium with iodide ion and iodine molecule (Atkins, et al. 2010).

$$H_2O_{2(aq)} + 3\,I^{-}_{(aq)} + 2H^{+} \rightarrow I_3^{-} + H_2O$$

$$I_2 + I^{-} \rightleftharpoons I_3^{-}$$

4.3.2 Potential reactions responsible for iodine generation

At pH 4-11, the perhydroxy radical formed during water radiolysis (water based dilute system) dissociates to give superoxide ion O_2^{-}, which is an oxidising radical

$$HO_2 \rightleftharpoons H^{+} + O_2^{-} \ldots\ldots a$$

Above pH 11, the hydroxyl radical and hydrogen peroxide dissociate to give the oxide ion and a peroxide ion, respectively,

$$^{\bullet}OH \rightleftharpoons H^{+} + O^{-} \ldots\ldots b$$

$$^{\bullet}OH + 2I^{-} \rightleftharpoons H^{+} + HO_2^{-} \ldots\ldots\ldots c$$

The hydronium ions generated in reactions a, b and c lead to the reaction between iodide and iodate to produce iodine. The concentration of hydronium ion generated during irradiation is optimum to carry out the iodide iodate reaction which usually takes place at low pH. This theory was confirmed by measuring the pH of irradiated solutions. The pH of solution changes gradually from alkaline (9.5-10) to neutral as radiation dose increases. Unirradiated solution has pH around 9.5 that decreases (due to the formation of hydronium ion through water radiolysis of dilute solutions) with increasing dose and reaches ph 7.1-7.3 after receiving 2500 Gy absorbed dose. For solutions irradiated to 6000 Gy the pH was almost 7 (Figure 4.11). This important observation has helped to understand and confirm the reaction mechanism proposed more clearly. Pulse radiolysis studies at nano second scale would be a better tool for understanding the reaction more clearly (Buxton, et al. 1988).

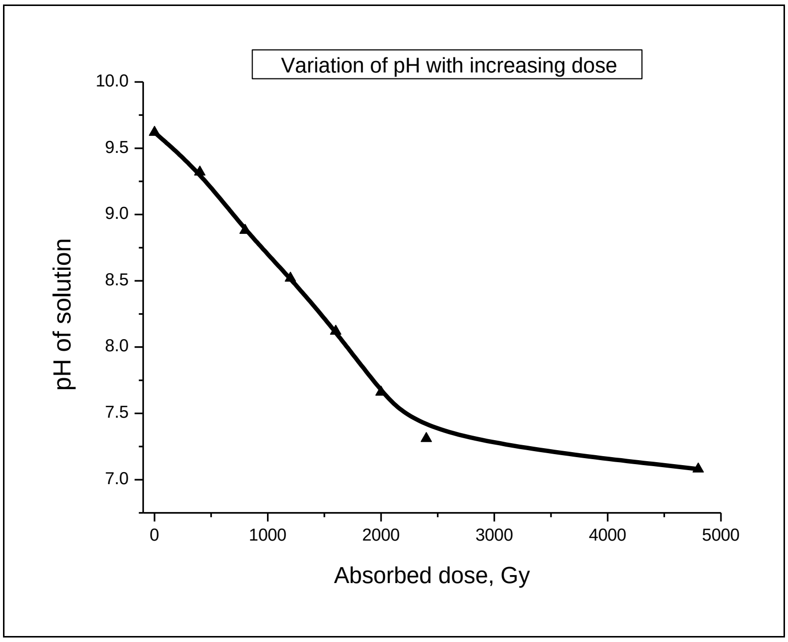


Figure 4.11: Graph depicting decrease in pH of solution with increasing absorbed dose

Many reaction mechanisms are known, reaction given below being the most widely used for representation (Xie, Michael and Margerum 1999)

$$IO_3^- + 5\,I^- + 6\,H^+ \longrightarrow 3\,I_2 + 3H_2O$$

The I-I bond is relatively weak, with a bond dissociation energy of 36 kcal/mol, and most bonds to iodine are weaker than for the lighter halides (Darwent 1970). One consequence of this weak bonding is the relatively high tendency of I_2 molecules to dissociate into atomic iodine. Iodine generated radiolytically is in excited state and easily dissociates into iodine atoms. Additionally there is small yield of iodine atoms generated directly from iodide ion.

$$^{\bullet}OH + I^{-} \rightarrow OH^{-} + I^{\bullet}$$

$$^{\bullet}OH + 2I^{-} \rightarrow OH^{-} + {}^{\bullet}I_2^{-} \text{(independent of pH)}$$

Reactiom mechanism are exerpted from the reference (Spinks and Woods 1990).

Iodide iodate reactions are predominant, leading to formation of iodine that reversibly gets converted to triodide in the presence of iodide ions. The iodine atom generated via radiolysis of iodate-iodide solution, adds to fluorescein at its electron rich centre, i.e. carbon positions close to hydroxyl group (Mc Cullagh and Kelly 2007) leading to iodination. The reaction continues at other carbon atoms in ortho position of the hydroxyl group. Thus mono, di, tri and finally tetra-iodo derivatives are formed. Decomposition of the carbonic acid by-product and release of carbon dioxide (from bicarbonate) drives the reaction to completion (Mc Cullagh and Kelly 2007). As the iodination continues, colour of the solution changes from fluorescent yellow in un-irradiated form to deep-red (cherry red) after receiving a dose of around 15 kGy.

Initial experiments were conducted with iodide salt along with carbonate, hydroxide and bicarbonate. The reason for choice of the reagents was based on studies conducted by researchers in different applications as quoted in preceding paragraphs earlier.

Iodine was generated in-situ by irradiating iodide-iodate solution in alkaline medium as explained in proposed reaction mechanism. Iodine formed along with bicarbonate present reacts with fluorescein to form erythrosine. The reaction is driven by decomposition of carbonic acid formed with release of carbon dioxide that leads to its completion.

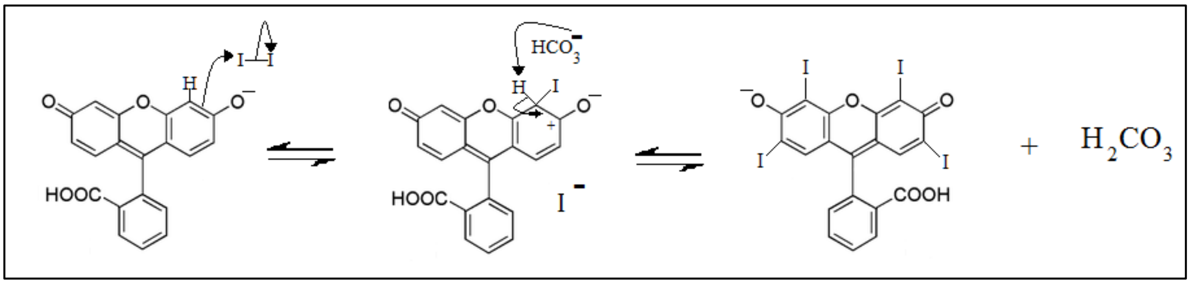


Figure 4.12: Reaction mechanism for iodination of fluorescein

The reaction mechanism shown in Figure 4.12 explains the role of bicarbonate in iodination reaction. Carbonic acid being unstable decomposes quickly to carbon dioxide and water. This carbon dioxide was detected when experiments were done in sealed plastic pouches. The tubes were filled such that no air bubbles were trapped inside (in a way similar to that for filling Fricke solution) and irradiated. There is formation of bubbles (carbon dioxide) during irradiation of the solution, thus confirming the role of bicarbonate in driving the halogenation reactions towards completion.

4.3.3 **Experimental details**

Initial experiments were performed using stoppered conical flasks made of glass that were cleaned by procedures mentioned for glass cleaning in experimental techniques. All irradiation were carried out at room temperature that varied between 22-35^{o}C. Irradiation was also done in plastic pouches and tubes that are cleaned using techniques mentioned for cleaning of polypropylene tubes. All polymer containers were preconditioned by filling them with distilled water and irradiating at a dose of about 500 Gy. Jasco V 530 UV/Vis double beam spectrophotometer was used for all absorbance measurements.

Experiments were performed to test the feasibility of the reaction as indicated in Table 4.3 and reagents are finalized. Sample solutions of iodide and iodate along with varying concentrations of uranine were irradiated in ^{60}Co gamma chambers to give gamma dose and measured spectrophotometrically. Sodium hydrogen carbonate was added at varying concentrations to study its influence on the reaction. pH of the solutions was varied from 8-14 to optimize the reaction. Concentration of reagents i.e. iodide, iodate, uranine and sodium hydrogen carbonate were also optimized. Effect of catalysts, di-sodium tetraborate decahydrate (borax) and ammonium orthomolybdate was studied separately.

4.3.3.1 **Reagents and Preparation**

Reagents involved are sodium hydroxide, uranine, bicarbonate, iodide, iodate, bromate, chlorate along with borax, ammonium vanadate and ammonium molybdate used as catalyst. All solutions were prepared using single distilled water. Stock solutions of reagents are prepared and kept in stoppered standard volumetric flasks in dark environment. Iodide and fluorescein solutions are prepared in small amounts and kept in dark refrigerated conditions owing to their sensitive nature. Trichloroacetic acid is extremely corrosive and emanates a acrid odour and therefore handled in fumehoods. Thick rubber gloves were worn during its handling. Carbondioxide released during addition of potassium carbonate to trichloroaetic acid was allowed to vent before stoppering the flasks to prevent accidental damage. Other chemicals are handled as per standard chemistry laboratory protocols.

4.3.3.2 **Irradiation and Measurement**

All irradiations were carried out in gamma chamber GC-900 and GC-1200. Spectrophotometric measurements were done after the solutions were diluted with distilled water to 50 % of their original concentration as their high optical density did not permit direct measurements. Most reported results are based upon visual observations.

4.3.3.3 **Determination of optimum composition**

The optimum composition of reagents involved are presented in Table 4.3.

Table 4.3: Initial experiments to check out feasibility to use as radiation indicator

Reagents	**Colour observed after irradiation**		
	Iodide(10 mol/m^3)- Iodate(5 mol/m^3)- Uranine(1 mol/m^3)	**Iodide(10 mol/m^3)- Bromate(5 mol/m^3)- Uranine(1 mol/m^3)**	**Iodide(10 mol/m^3)- Chlorate(5 mol/m^3)- Uranine(1mol/m^3)**
NaOH (**5mol/m**^{3})	Dark red after 100 kGy dose	Dark pink after 100 kGy dose	No Change
Glycerine (1%) - K_2CO_3(**2mol/m**^{3})	Light red after 50 kGy dose	No Change	No Change
$NaHCO_3$ (**15 mol/m**^{3})	Red after 50 kGy dose	No Change	No Change
K_2CO_3 (**20mol/m**^{3})	Orange red after 50 kGy dose	Orange after 25 kGy dose followed by decolourisation	No Change
K_2CO_3(20**mol/m**^{3}) – Trichloroacetic acid (**2mol/m**^{3})	Orange red after 15 kGy dose	Orange pink after 5 kGy dose and thereafter decolourisation	Orange after 5 kGy dose

N.B.: Concentrations of reagents are based on achieving solution of pH 10

Table 4.4: Effect of trichloroacetic acid

Reagents	**Iodide(10 mol/m^3)-Iodate(5 mol/m^3)-Uranine(1 mol/m^3)-NaOH (5mol/m^3)**
K_2CO_3 **(20mol/m^3)-** Trichloroacetic acid **(2mol/m^3)** - $NaHCO_3$ **(15mol/m^3)**	**Colour observed after irradiation**
	Red after 5 kGy dose

4.3.4 Results and Discussions

Initial experiments were carried out using sodium hydroxide to adjust the pH around 10 so as to achieve sufficient phenoxide ion formation, which is expected to drive the reaction. It was observed that although the phenoxide ion is formed, due to high pH the activity of iodine was reduced leading to colour change only at high radiation doses. 1 mol/m^3 solutions of bromate and chlorate were added as higher halogens oxides to induce iodination. However, chlorate in general did not produce any visible colour change.

Bromate did give positive results, however the threshold dose was found to be too high. Erythrosine formation was found to be maximum for iodate based system. Thus, iodate was chosen as preferred oxidizing agent. Glycerine is known to absorb large quantities of nascent iodine (Hartshorne 1865), hence it was added; so as to dissolve any iodine released during irradiation would be available as soluble iodine for iodination reactions. Glycerine was found useful in iodination reactions however the threshold dose is higher than that observed for bicarbonate. Potassium carbonate is known to drive halogenation reactions in electro chemical methods (Vasudevan and Ananthraman 1994) for production of erythrosine; it was tested for its ability to aid in radiation chemical synthesis. Aqueous solutions of trichloroacetic acid produce chlorine radicals and hydrogen chloride when irradiated by UV (Gara, Bucharsky and Wörner 2007) as well as gamma radiation (Kuroda, et al. 2003); (Saion, et al. 2004). Trichloroacetic acid was introduced into the system, so that the acid formed due to radiolysis of the former would lead to increase in rate of iodide iodate reaction, thus improving iodine formation. Trichloroacetic acid was experimentally found to sensitize the system by lowering the threshold dose for erythrosine formation (Table 4.4). Trichloroacetic acid is dissolved in potassium carbonate solution (neutralisation) before introducing in solutions, as it is highly acidic and leads to precipitation of uranine as fluorescein and evolution of iodine. Sodium bicarbonate was found to be the best among the reagents tried for the iodination reactions. In presence of bicarbonate the reactions reached completion with lower dose as compared to other reagents used in the experiments. Trichloroacetic acid enhances the yield of sodium bicarbonate driven iodination reactions by virtue of acid formation and can be used to enhance the erythrosine formation to a great degree.

To confirm the interdependence of iodate and iodide, experiments were performed with individual reagent and their combinations. Results indicated that both iodide and iodate are required for the reaction to occur (Table 4.5). The components used are uranine, iodide, iodate, and sodium bicarbonate in alkaline medium (NaOH). Experiments were performed with no alkali (sodium hydroxide) added as uranine and bicarbonate solutions are fairly akaline. It was observed that the threshold dose for erythrosine formation is reduced; however the role of alkali in reaction mechanism is not ruled out (Table 4.6). Uranine (1 mol/m^3) along with bicarbonate (5 mol/m^3) in distilled water, generates a solution of pH 9.5-10.Figure 4.13 presents the radiation chemical reaction mechanism for erythrosine synthesis.

Table 4.5: Results of experiments performed to establish role of Iodide and Iodate

Reagent	**Colour observed after 15 kGy dose**		
	Iodate(10 mol/m^3)	**Iodide(20 mol/m^3)**	**Iodide(20 mol/m^3)-Iodate(10 mol/m^3)**
NaOH (5mol/m^3) - Uranine(1 mol/m^3) - NaHCO$_3$(5 mol/m^3)	Solution remained fluorescent	Solution remained fluorescent	**Turned Red**

Table 4.6: Results of experiments performed without sodium hydroxide

Reagent	**Colour observed after 10 kGy dose**
Iodide(20 mol/m^3)-Iodate(10 mol/m^3)Uranine (1 mol/m^3) - NaHCO$_3$(5 mol/m^3)	**Turned Red**

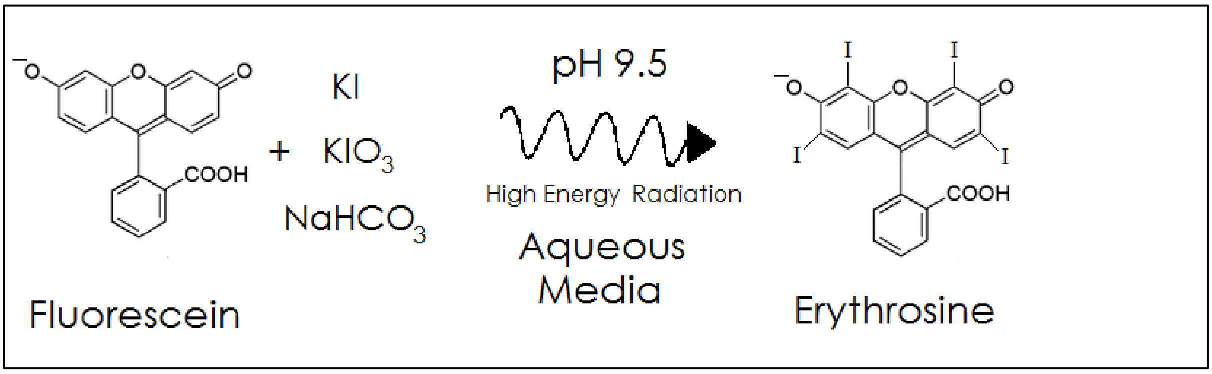


Figure 4.13: Radiation chemical synthesis of Erythrosine

Tricholoroacetic was added to prove the role of acid formed during radiolysis in enhancing the reaction yield. Milder and less toxic reagents like borax were tested for their role as catalyst in the system so as to avoid relatively hazardous trichloroacetic acid (Li, et al. 2011).

Effect of selected catalysts was studied on the product formation through the oxidation of iodide-iodate to iodine is presented in Table 4.7.Concentrations of 5 mol/m^3 borax, vanadate and molybdate were used separately to investigate their effect on the discussed radiochromic system. Borax reacts with hydrogen peroxide generated by water radiolysis to form perborate as shown in Figure 4.14 and Figure 4.15. Perborate along with radical species generated oxidise iodide-iodate to iodine (Kolbl and Schmidt-Lehr 2010).

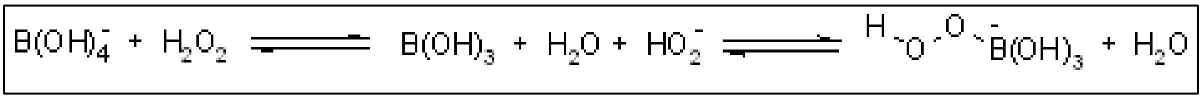


Figure 4.14: Formation of perborate during water radiolysis

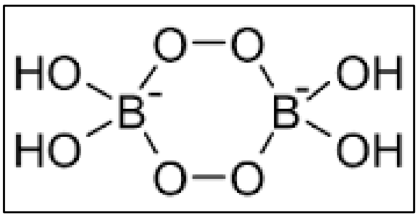


Figure 4.15: Structure of Perborate

In the experiments conducted, borax was found to enhance the reaction rate with the dose required to be less than 2.5 kGy.

Molybdate, a well-known catalyst for halogenation reactions in organic compounds (Singh and Agarwal 2014) showed similar catalytic effect in the iodination reactions. The catalytic effect of ammonium orthomolybdate was seen to be greater than borax. A radiation dose less than 1kGy was required for the molybdate added system for complete iodination of fluorescein.

Table 4.7: Results of experiments to study the effect of catalyst on reaction mechanism

Reagent	**Vanadate** **(5 mol/m^3)**	**Molybdate** **(5 mol/m^3)**	**Borax** **(5 mol/m^3)**
Iodide(20 mol/m^3)-Iodate(10 mol/m^3)-Uranine (1 mol/m^3) - NaHCO$_3$ (5 mol/m^3)	Turned Red within7.5 kGy dose	Turned Red within 1kGy dose	Turned Red within 2.5 kGy dose

Vanadates were found to have least catalytic effect, compared to borate and molybdate ions. The probable reason may be due to multiple oxidation states exhibited by vanadium. It is proposed that hydrogen peroxide formed during water radiolysis along with other oxidising species produced lead to iodine formation in iodide-iodate solution. These oxidising species are utilised by vanadium to oxidise to higher oxidation states as vanadium compounds are easily oxidised. Depending on the experiments the reactants were finalized to optimize the reactions.

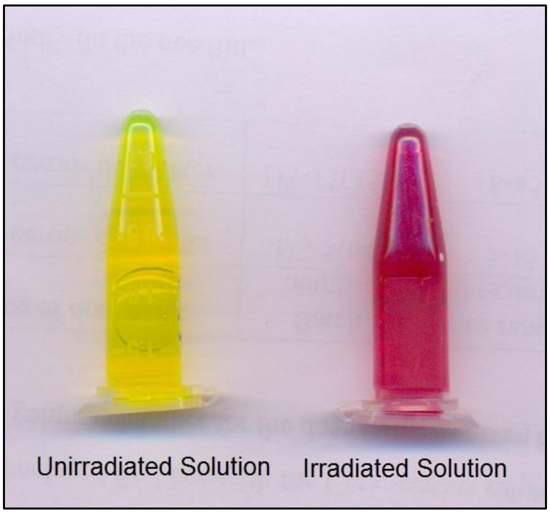


Figure 4.16: Formation of erythrosine from fluorescein after receiving 10 kGy dose (non catalysed system)

Thus, a final concentration of 20 mol/m^3 of iodide, 10 mol/m^3 iodate, 1 mol/m^3 of fluorescein and 5 mol/m^3 of bicarbonate was fixed to for the system to be used as radiation processing indicator solution. Fairly alkaline solution (pH 9-10) was required to create a balance between fluorescein solubility and iodide iodate reaction. Molybdenum and borax, used as catalysts were found to improve the rate of reactions to a great extent. Formation of mono, di and tri-iodofluorescein in the intermediate stages can be observed at their respective wavelengths of maximum absorption. Uncatalysed solutionwas irradiated to dose of 10 kGy (Figure 4.16) and deposited drop wise on Whatman chromatography paper. The paper was observed under UV light for detecting fluorescence due to presence of fluorescein, as no fluorescence was visually observed the iodination reaction can be said to be complete. This was also confirmed by spectrophotometry measurements (Figure 4.17).

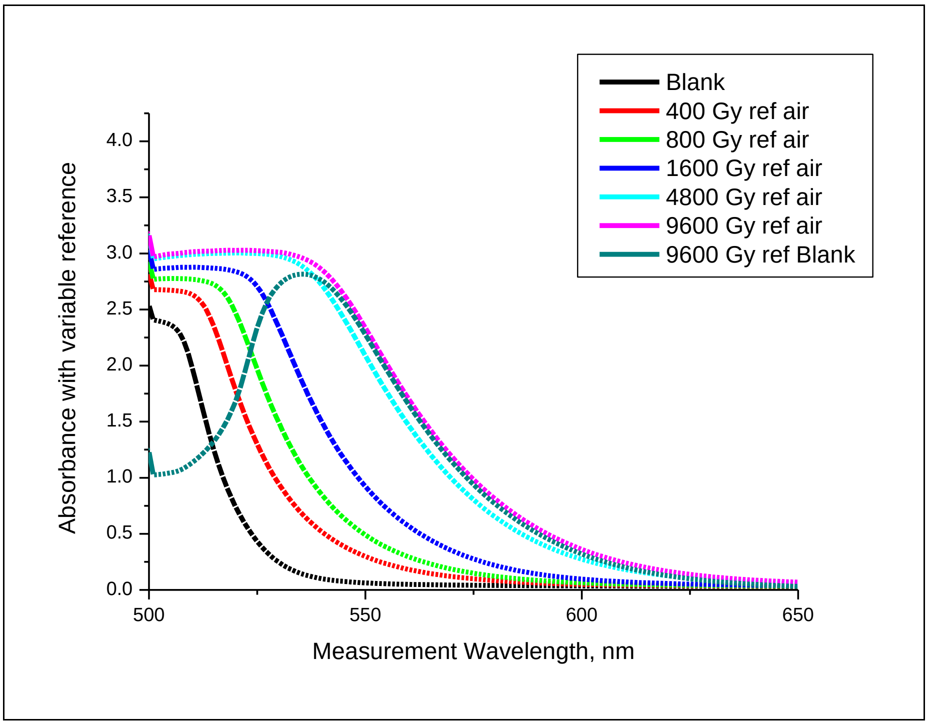


Figure 4.17: Comparative spectra of irradiated solution (50% dilution) with un-irradiated control

4.3.5 **Conclusions**

A new technique for radiation chemical synthesis erythrosine from fluorescein is developed (S. G. Mhatre, et al. 2016). Further, use of this reaction for development of radiation processing indicator is discussed. In the first step, iodide is oxidised to iodine with the help of iodate, and prescence of bicarbonate helps in completion of the reaction. Borax and molybdate were found to increase the reaction rate and thus used as catalysts. Trichloroacetic acid was also found to improve the erythrosine yield. Thus, with the help of radiation, contaminant free erythrosine can be synthesised from fluorescein. The method eliminates use of iodine and caustic chemicals.20 mol/m^3 of iodide, 10 mol/m^3 iodate, 1 mol/m^3 of fluorescein and 5 mol/m^3 of bicarbonate are the final reagent concentrations to be used for preparation of radiochromic solution. The solutions can be prepared easily and filled in plastic pouches or tubes before irradiation. Storage of solutions should be preferably done in stoppered glass containers in refrigerated conditions. The developed radiochromic solution is fluorescent yellow in unirradiated form that gradually changes to shades of yellow on receiving dose greater than 200 Gy on further irradiation (5 kGy dose) the solution becomes orange. The colour deepens in shades of orange with further irradiationto finally become red after receiving 10 kGy dose. The colour change associated with irradiation can serve as an indicator of the dose received by the solution and thus be implied to the approximate dose received by adjoining irradiated sample. The radiation indicator liquid can be readily used (without any further modifications) in radiation sterilization of medical products where minimum dose required for sterilization is 25 kGy. The indicator liquid will turn red after receiving 10 kGy dose and continues to remain red upto 40 kGy. After 40 kGy, colour of the solution becomes light red and on further irradiation becomes colourless. In conclusion, radiation sterilization can be confirmed by observing the colour produced. Alternatively sodium hydroxide or similar alkali can be added to achieve colour formation at desired dose.

The developed radiation indicator liquid is ready to be used commercially. The radiation indicator solution can be used for experiments and demonstrations to research students as an inexpensive replacement for radiation indicator.

Additionally new radiation chemical technique for erythrosine synthesis has been found. The developed techniques can be scaled up for commercial manufacture of the dye using radiation technology. The proportions of the reagent should be in the ratio found during experimental work for obtaining optimum yield.

4.4 Radiochromic Dosimeter

In India, for low dose applications Fricke dosimeters are used to cover dose range from 30-350 Gy. These applications include potato onion and tuber irradiation for shelf life extension. While Ceric cerous dosimeter is used for medium dose applications as it covers a wide range from 1000 Gy to more than 50 kGy using different concentrations (discussed in introduction). Measurement of dose in the range of 400 Gy to 1000 Gy is performed using imported dosimeters such as radiochromic waveguide dosimeter and radiochromic films. These dosimetric systems are expensive and their availability is limited due to their foreign origin. Presently indigenous dosimeters in the dose range of 400 Gy to 1000 Gy are not available commercially; therefore an attempt was made to indigenously develop dosimeters especially in this range.

Radiochromic systems have wide applications in radiation industries, medical sciences, health physics and radiation dosimetry. Various developmental stages of radiochromic dosimetry in mGy to MGy range depending on its applications in radiation processing industries, radiological safety, medical sciences, nuclear or dirty bomb exposition and radiation accident have been developed. Leuco dyes, pH sensitive dye with halogen containing compound and radiation induced solid state polymerization are the basic chemical methods presently in use for radiochromic techniques (Vaijapurkar and Bera 2010). A few dosimeters cover the above mentioned dose range, FWT -70 is one of the few. The FWT-70 series of dosimeters use hexa (hydroxyethyl) aminotriphenylacetonitrile (HHEVC) dye inside an optical waveguide. Readout of the dosimeters is by photometric means using dual wavelength photometry. The Color development time is 1 hour, and is sensitive to UV lights wavelengths less than 350 nm. With a shelf life of less than 24 months at optimal storage temp of 4 ºC, the US based dosimeters are available to us at a market price of Rs 400/- . In addition, the dosimeters cannot be read in a normal spectrophotometer, a specially designed unit to measure the absorbance has to be purchased separately (4-5 lakh rupees) along with the dosimeters. The maintenance and operating cost of dosimetry system, thus adds to the radiation processing cost. The FWT -70 dosimeters contain toxic cyanides that are hazardous to life and dangerous to environment. In view of the high cost, sanctions affected purchases, toxicity of the dosimeters, and specific requirement of sophisticated equipment, indigenous system need to be developed.

Radiation chemical synthesis of erythrosine was optimized in the earlier experiments, along with its use as radiation processing indicator. Its application as radiochromic dosimeter for routine dosimetry in radiation processing facilities is discussed in this section. Formation of erythrosine from fluorescein occurs in steps that can be observed as the gradual change in colour of the solution with increasing dose. The solution based indicator is water equivalent as dilute solutions of millimolar concentrations are used.

4.4.1 **Principle**

Section 4.3.1 gives the principle involved in detail.

4.4.2 **Experiment Details**

Polypropylene tubes were used as sample solution containers, kept in 10% nitric acid for 24 hours for degreasing. The de-greased tubes were successively washed with tap and distilled water. Containers were preconditioned by filling them with distilled water and irradiating at a dose of about 500 Gy. Jasco V 530 UV/Vis double beam spectrophotometer was used for all absorbance measurements.

Concentration of reagents i.e. iodide, iodate, uranine and sodium hydrogen carbonate were optimized along with effect of catalyst studied separately. Pre and post irradiation stability were studied. Effect of reagents on improving the Pre and post irradiation stability is also discussed in detail. Optimization of wavelength measurement and final establishing the system as a dosimeter is explained.

4.4.2.1 **Reagents and Preparation**

Reagents are prepared in similar manner, as explained earlier during development of radiation indicator liquid. Additionally stock solutions some reagents like sulphite, bisulphite and thiosulpite are either prepared fresh or added in solid form to solutions as per standard chemistry laboratory chemicals preparation protocols.

4.4.2.2 **Irradiation and Measurement**

It is important that the same position of gamma chamber is used for irradiation, as variation in dose rate spatially can affect the dose received. In all cases the central volume of gamma chambers is chosen as it is expected to have maximum uniformity. Proper Build up for electrons is provided so as to avoid dose due to secondary electrons. As the tubes are machine made and polished with grease they are degreased by following standard procedures mentioned earlier in Chapter 2. Polypropylene tubes were used as sample solution containers. Irradiation Preconditioned Containers were by filling them with sample solution and all measurements were carried out at 25 °C. Alternatively Polythene bags (2 cm X 2 cm) and polypropylene centrifuge tubes (5 ml capacity) were used for containing liquids. The cleaning procedure is same as that described earlier for solution containers.

4.4.2.3 **Determination of optimum composition**

Concentration of components iodide, iodate, uranine and sodium hydrogen carbonate was fixed using concentration dependence study. The concentrations of reagents used for primary investigations are based upon the studies carried out during development of radiation indicator solution. In concentration dependence study, solutions with 1 mol/m^3 of uranine, 10 mol/m^3 iodate, and 5 mol/m^3 of bicarbonate were prepared with varying concentrations of iodide in separate containers. The solutions are irradiated and measured spectrophotometrically. The exercise gives the optimum concentration of uranine to be used. The exercise was repeated for bicarbonate, iodide and iodate. The entire exercise was repeated for finalizing the concentration of other reagents. Effect of catalysts, di-sodium tetraboratedecahydrate (borax) and ammonium orthomolybdate was studied separately. Pre irradiation effect, post irradiation effect, dose rate effect, dose fractionation effect and reproducibility studies were conducted with non-catalysed solutions (borax or molybdate not added).

4.4.2.4 **Dose Rate and Dose Fractionation Effect**

To study the effect of dose rate on the system, solution samples were irradiated to three different doses in GC-900 and GC-1200 having dose rates of 10 Gy/min and 40 Gy/min, respectively. Solutions were irradiated to three doses so as to cover the entire dose range. Dose is fractionated into two equal doses with a gap of 30 minutes and 60 minutes between irradiations to simulate conditions of break down in radiation processing facilities.

4.4.2.5 **Pre- and Post- Irradiation Stability**

For pre irradiation stability study, containers of freshly prepared solutions were covered with aluminium foils (to avoid light exposure) and kept at standard laboratory condition (room temperature); absorbance was measured immediately after the solution is prepared. For post irradiation stability study, solution was irradiated to known doses. Absorbance of the irradiated solutions was recorded as soon as irradiation is complete under controlled conditions (25°C). Reproducibility study was carried out by irradiating ten different samples to lower and upper limits of dose range.

4.4.3 **Results and Discussions**

The optimum composition of radiation indicator solution was established in two different ways. In the first set of experiments iodide & iodate concentrations were varied as shown in Figure 4.18 and Figure 4.19**.**

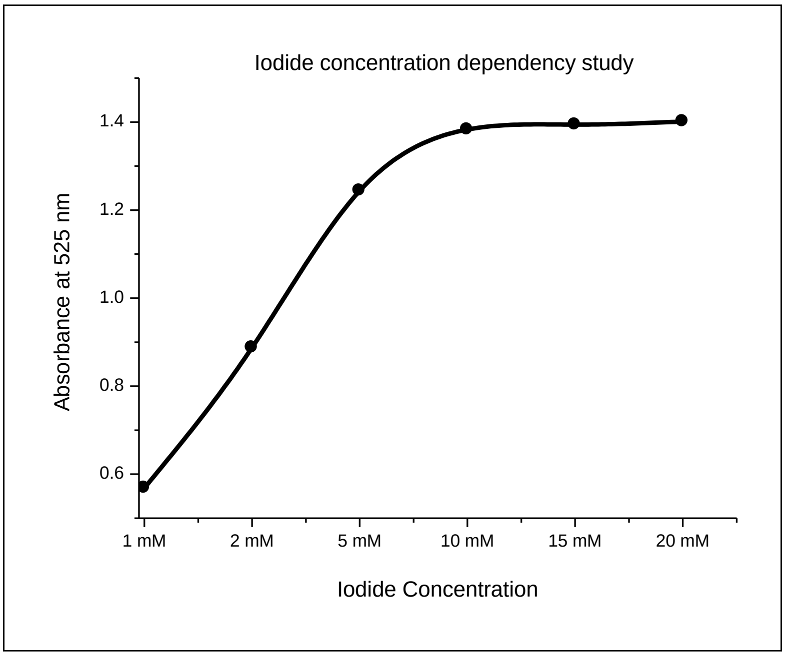


Figure 4.18: Optimum concentration- iodide

In concentration dependence study, iodide and iodate concentration were first to be fixed as they decide concentration of iodine produced. Sodium bicarbonate is radiolytically inert, but plays a major role in reaction completion so its concentration is fixed after iodide and iodate. Phenolic groups of fluorescein make it less reactive towards free radicals generated by water radiolysis and its concentration dependence was studied after fixing all other reagent concentrations.10 mol/m^3 iodide and 5 mol/m^3 iodate concentration were found to be optimum from the experiments conducted.

Concentrations greater than this will not have a pronounced effect on the system individually, however if proportion of 2:1 iodate to iodide is maintained, proportionate increase in iodine formation was observed. Lower concentrations have an observable effect on system and should be avoided under all circumstances.

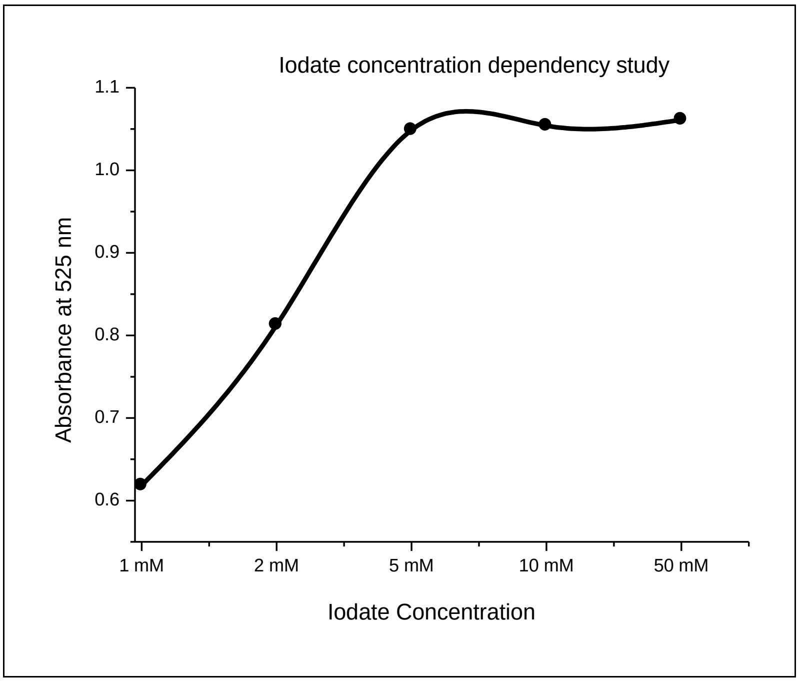


Figure 4.19: Optimum concentration-iodate

Optimum concentration of uranine is shown in Figure 4.20 and sodium hydrogen carbonate in Figure 4.21.

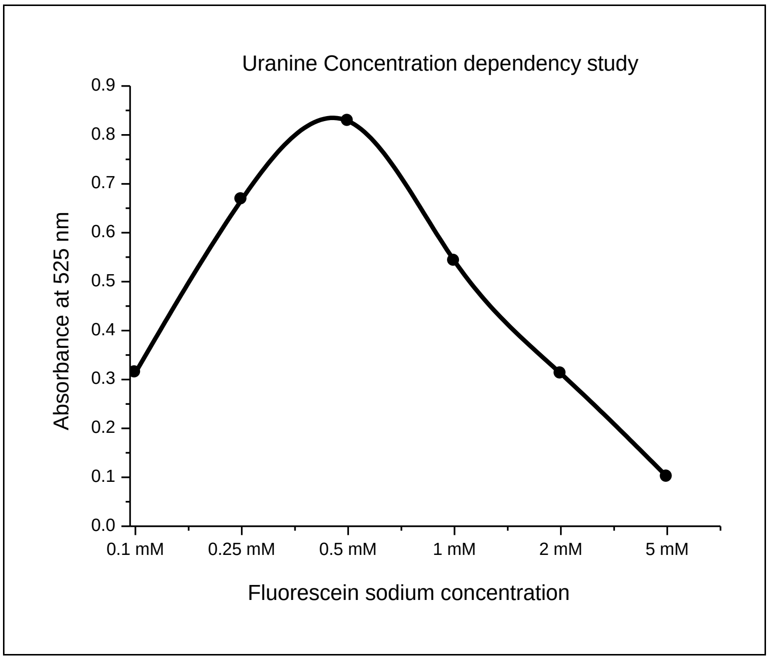


Figure 4.20: Optimum concentration- Fluorescein sodium

Uranine concentration below 0.5 mol/m^3 leads to underutilization of iodine formed while higher concentrations lead to incomplete iodination as observed experimentally.

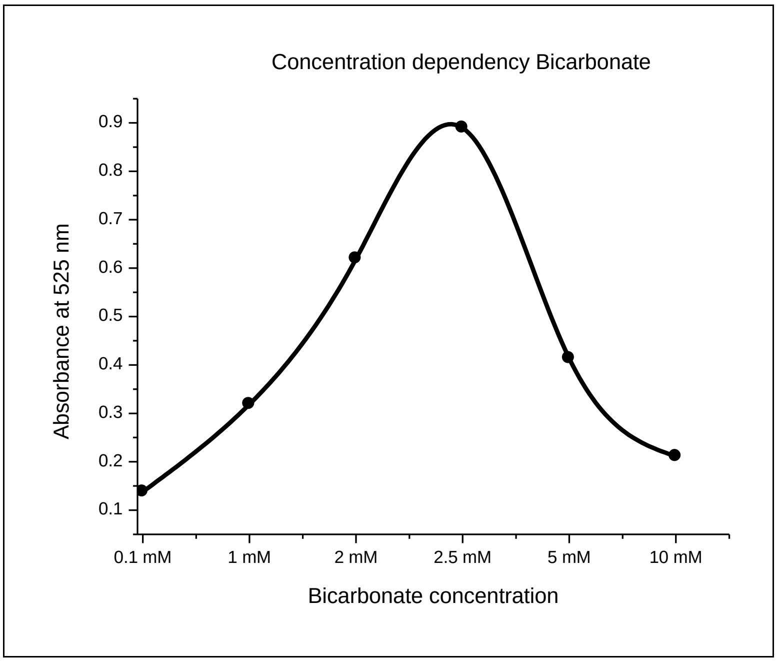


Figure 4.21: Optimum sodium bicarbonate concentration

Sodium carbonate concentrations above 2.5 mol/m^3 decrease the erythrosine yield as observed in graph above (Figure 4.21).

Choice of measurement wavelength

Absorbance of the irradiated solutions was measured as spectra. It was experimentally observed, that the wavelength of maximum absorption (λ_{max}) shifts from 522 nm to 545 nm,Figure 4.22. Change in wavelength is majorly attributable to different stages of iodination along changes in pH occurring with iodination reactions (Sjoback, Nygren and Kubista 1995).

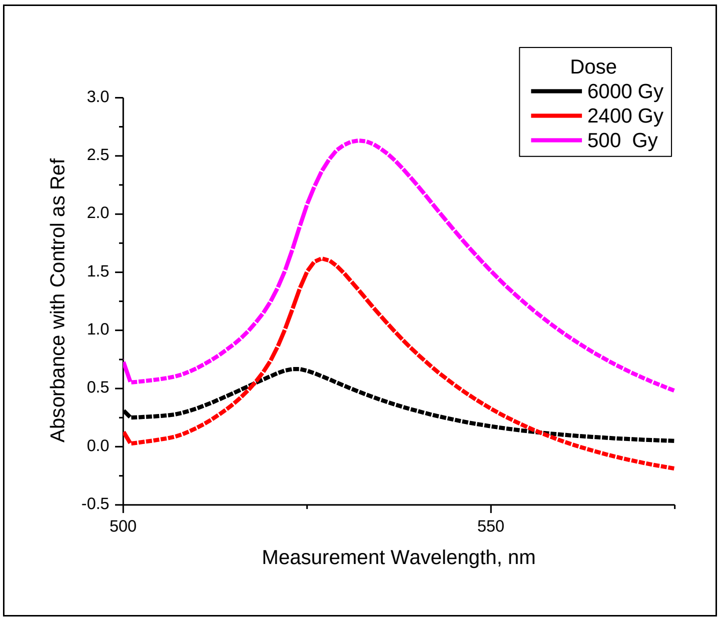


Figure 4.22: Change in wavelength of maximum absorption with dose (iodination)

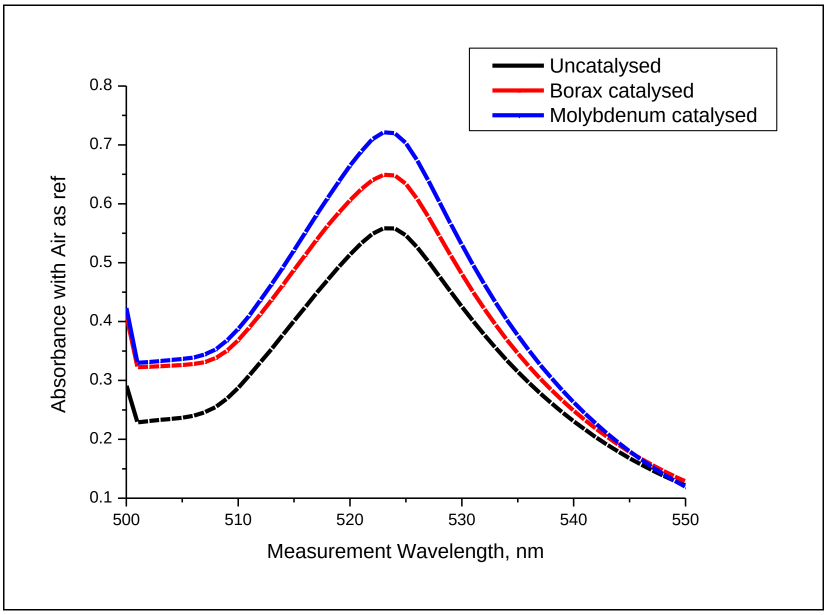


Figure 4.23: Comparative spectra of non catalysed and catalysed systems

Lower doses can be detected by using the maximum absorbing wavelength. Mono-iodofluorescein is the first derivative to be formed after irradiation. Maximum absorbance was recorded at 525 nm i.e. λ_{max} of mono-iodofluorescein.Comparative spectra of non-catalysed and catalysed systems (Figure 4.23) unanimously indicate 525 nm as the wavelength of maximum absorption. Therefore, 525 nm was chosen as analysis wavelength for all further spectrophotometric measurements.

2000 Gy is the saturation dose for all spectrophotometric measurements as above 2000 Gy, the increase in absorbance is very small with respect to the dose received. Also, the absorbance reaches a value of 2.5 beyond which absorbance measurements are not recommended (Figure 4.24).

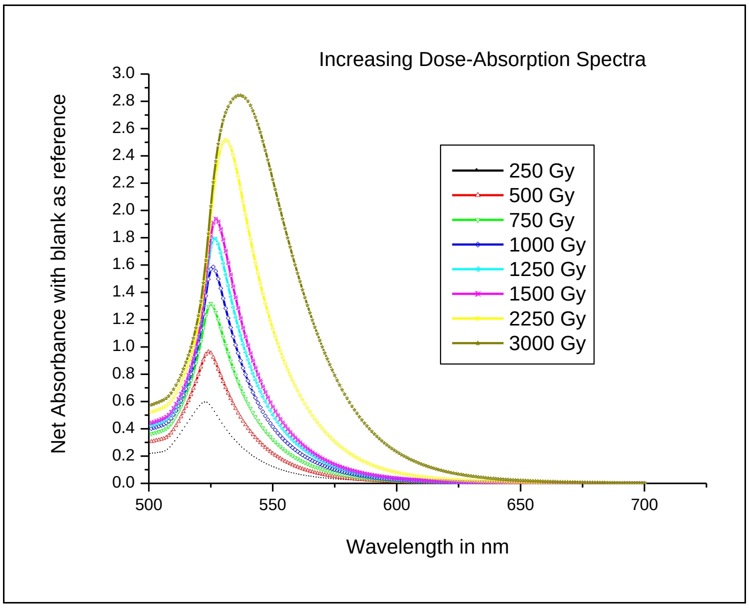
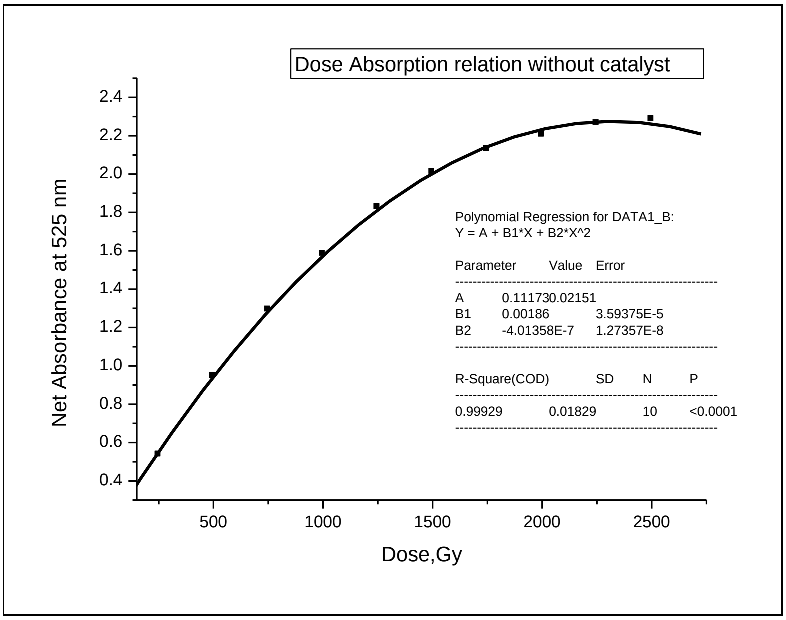


Figure 4.24: Spectra of irradiated solution irradiated to increasing doses



```
Polynomial Regression for DATA1_B:
Y = A + B1*X + B2*X^2

Parameter         Value    Error
------------------------------------------------------------
A           0.111730.02151
B1          0.00186          3.59375E-5
B2          -4.01358E-7      1.27357E-8
------------------------------------------------------------

R-Square(COD)                SD         N          P
------------------------------------------------------------
0.99929          0.01829             10         <0.0001
------------------------------------------------------------
```

Figure 4.25: Dose absorption relation for bicarbonate system without catalyst

Dose absorbance relation for bicarbonate system without catalyst shows second order fit using 525 nm at analysis wavelength (Figure 4.25). The measurable dose range is from 250 Gy to 2000 Gy. Beyond 2000 Gy the increase in absorbance values is very small compared to the dose absorbed.

5 mol/m^3 concentrations of borax and molybdenum were used separately to study their effect on the above system. Lower dose can be measured using molybdate catalyst as compared to equal concentration of borax.

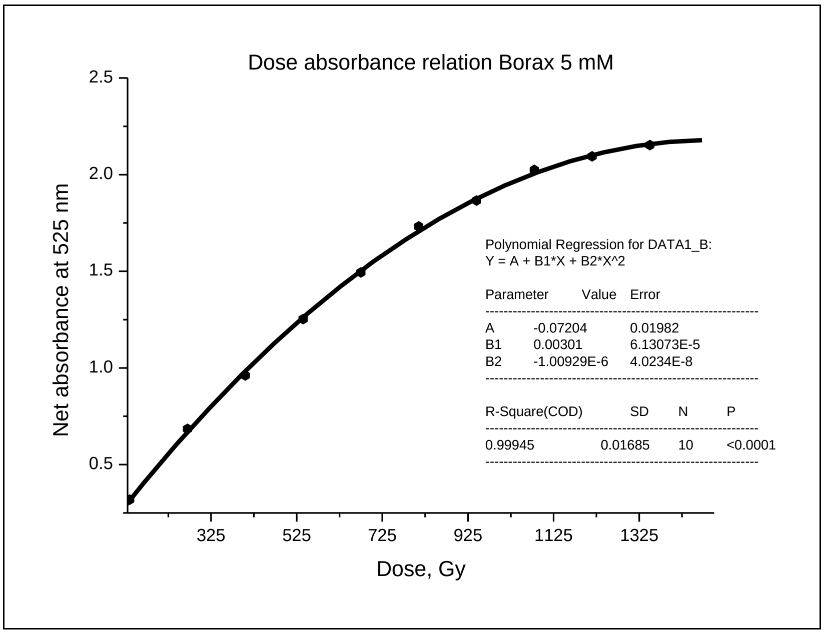


Figure 4.26: Dose absorption relation for bicarbonate system with borax as catalyst

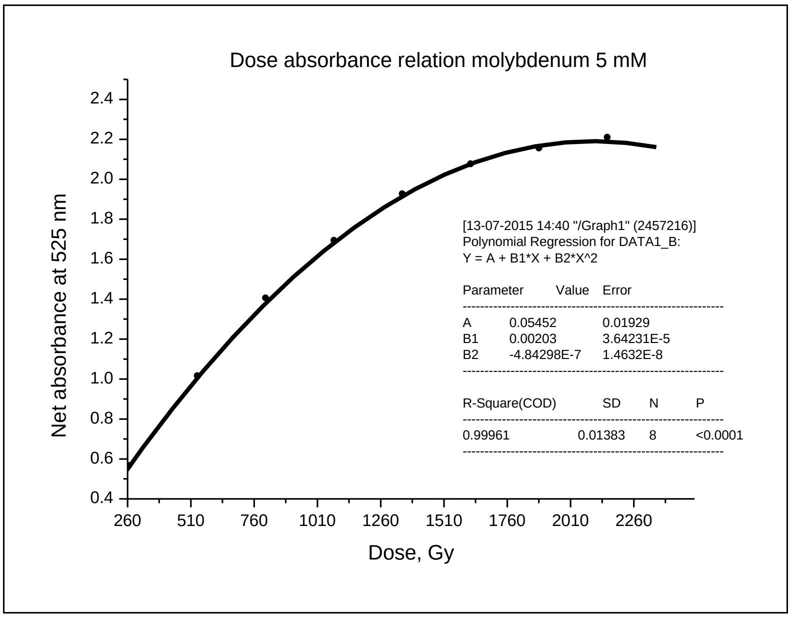


Figure 4.27: Dose absorption relation for bicarbonate system with molybdenum as catalyst

Figure 4.26 and Figure 4.27 represent the dose absorbance relation of the bicarbonate system with borax and molybdenum, respectively.

Pre- irradiation stability study

The pre irradiation stability study was performed for all the three systems (non catalysed, borax catalysed and molybdenum catalysed). For non-catalyzed system, a continuous increase in absorbance was observed shown in Figure 4.28 indicating instability probably due to iodine (generated thermally) reacting with fluorescein.

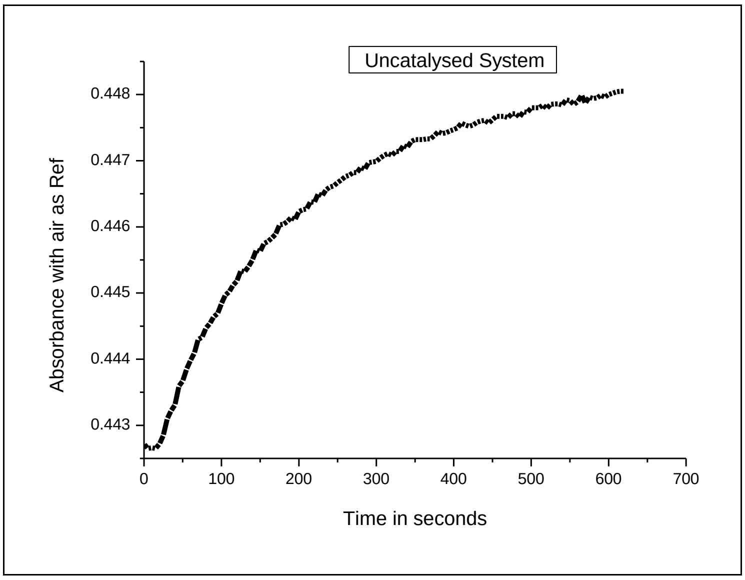


Figure 4.28: Pre- irradiation time dependence study of uncatalysed system

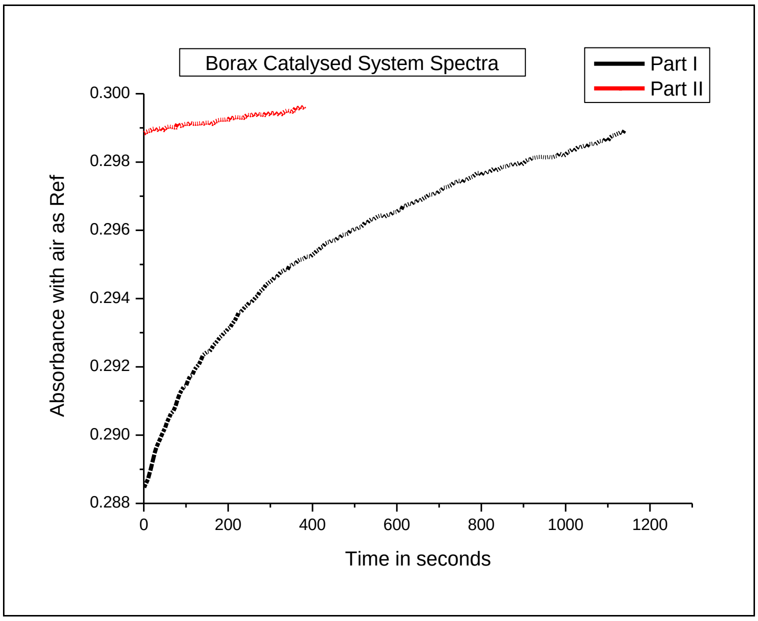


Figure 4.29: Pre- irradiation time dependence study of borax catalysed system

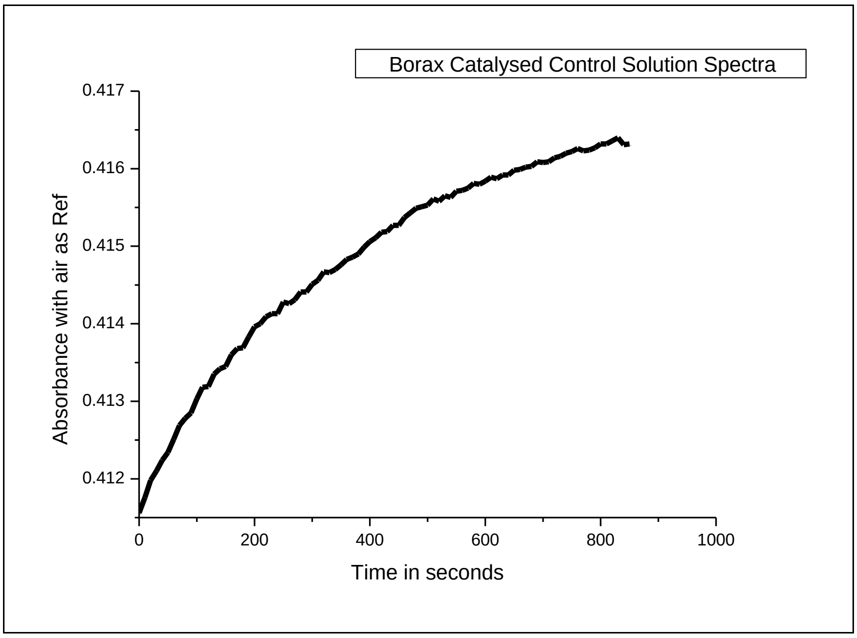


Figure 4.30: Pre- irradiation time dependence study of borax catalysed system after a gap of 60 min as continuation of earlier graph

For borax catalyzed system (Figure 4.29), the increase in absorbance is rapid upto 20 minutes from time of solution preparation after which it seemed to stabilise with time, however the increase continues as observed experimentally (Figure 4.30). Molybdenum catalysed solutions have the least stability; absorbance increases rapidly with time and continues to rise even after 24 hours of solution preparation.

The rise in absorbance can be attributed to (thermal and atmospheric) oxidation of iodide to iodine and its subsequent reaction with fluorescein. The reaction given below shows oxidation of iodide ions by ozone present in air.

$$2I^- + H_2O + O_3 \rightarrow 2OH^- + I_2 + O_2$$

To improve the pre irradiation stability, some experiments were performed. Fluorescein concentration was doubled (1 mol/m^3) in order to increase the reaction centres available to iodine generated thermally. However there was steady drop in absorbance value of the solution with time (Figure 4.31)

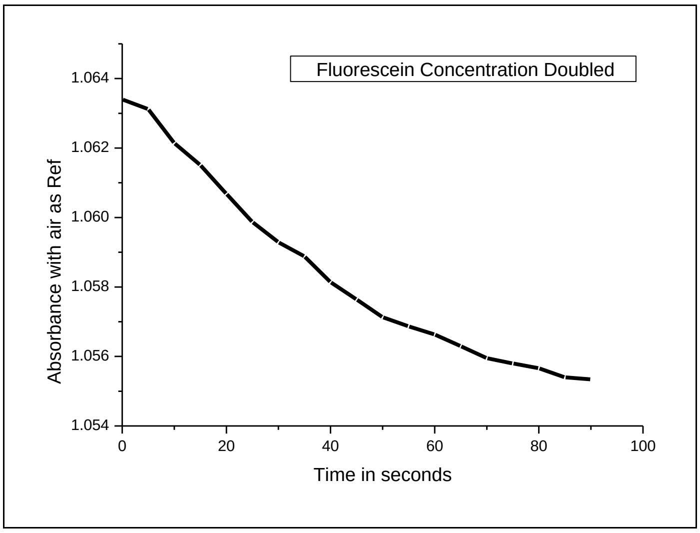


Figure 4.31: Pre- irradiation time dependence study of uncatalysed system with 1 mol/m^{3}Fluorescein concentration (double)

As alkaline medium (pH 11) lowers the iodide activity in solution, sodium hydroxide was added to reduce the oxidation of iodide. However at higher pH, the absorbance values change in cyclic way, alternating decreasing and increasing with time (Figure 4.32). The initial rise may be due to the phenoxide ion formed readily favouring iodination reactions leading to increase in absorbance followed by decrease in absorbance with time as iodine activity is reduced at high pH and reversible nature of iodination reactions.

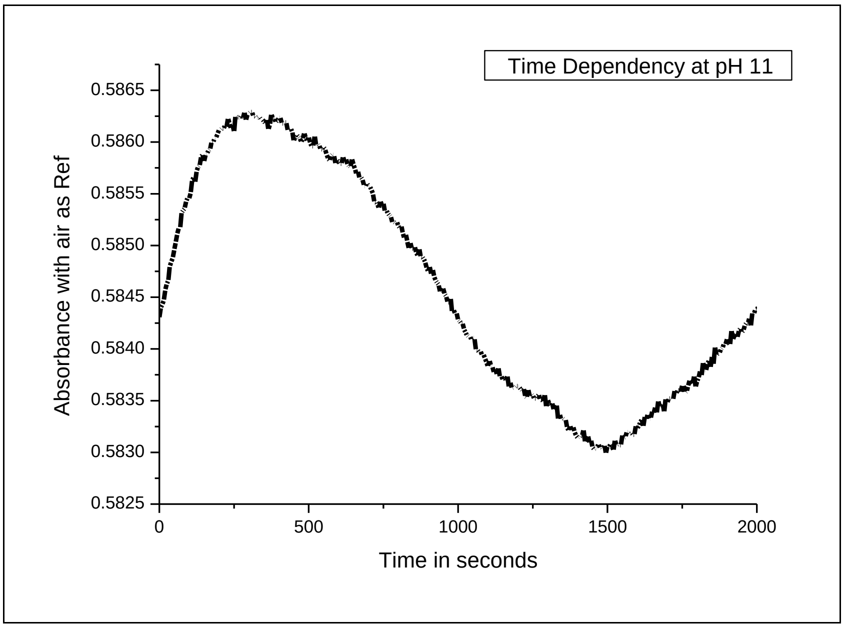


Figure 4.32: Pre- irradiation time dependence study of uncatalysed system at pH 11

Ammonium ions are easily oxidisable ions, ammonium carbonate was added to the system to as source of ammonium ions with additionally raising the pH of solution. However ammonium carbonate was not effective in stabilizing the system (Figure 4.33).

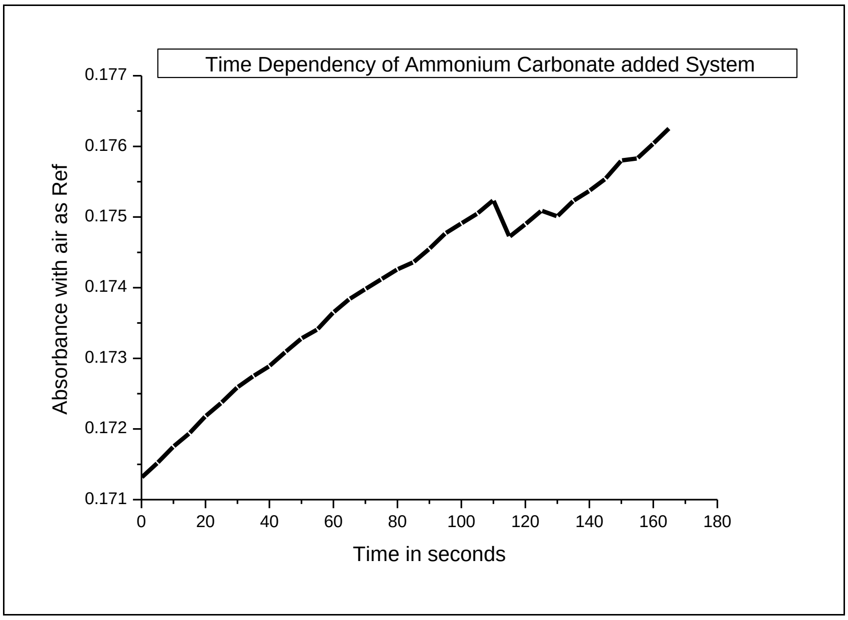


Figure 4.33: Pre- irradiation time dependence study of ammonium carbonate added uncatalysed system

Glycerine (known to absorb iodine in solution form) (Lee 1941) was added in an attempt to absorb iodine formed before irradiation. Solutions with glycerine were irradiated to observe any change in the absorption spectrum due to its presence (Figure 4.34). The post irradiation spectrum was similar to that obtained without glycerine (Figure 4.35), however glycerine did not improve the pre irradiation stability.

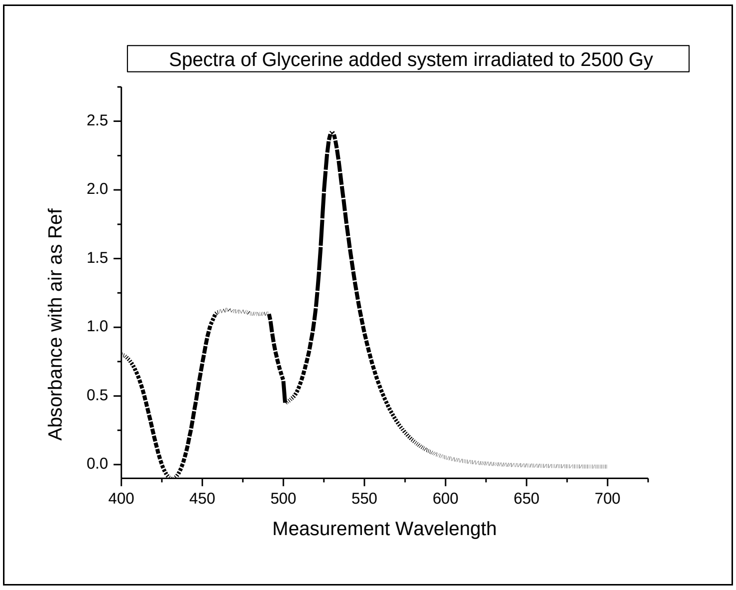


Figure 4.34: Post-irradiation spectrum of glycerine added uncatalysed system

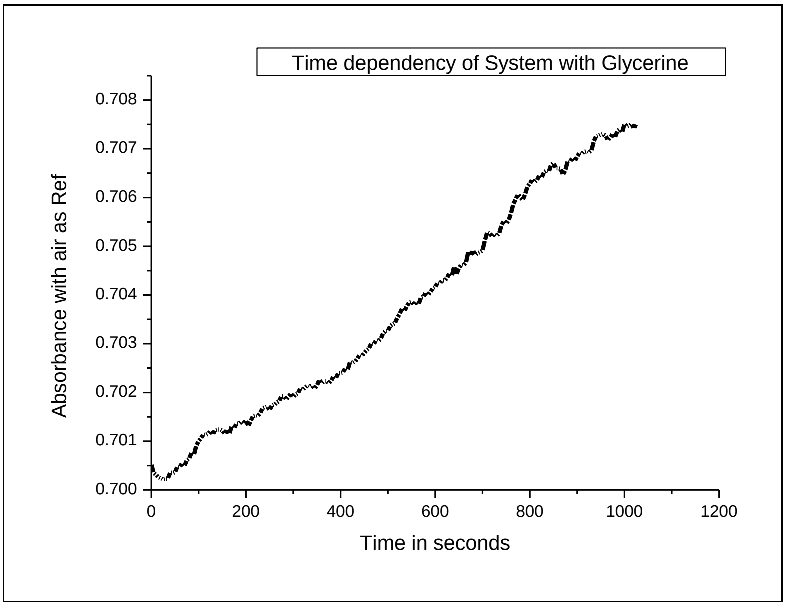


Figure 4.35: Pre- irradiation time dependence study of glycerine added uncatalysed system

Chlorate is a powerful oxidizing agent; it was expected to compete with oxidation reactions. Chlorate (1 mol/m^3) was added to the system but the absorbance increased steadily thus having no effect on stability (Figure 4.36)

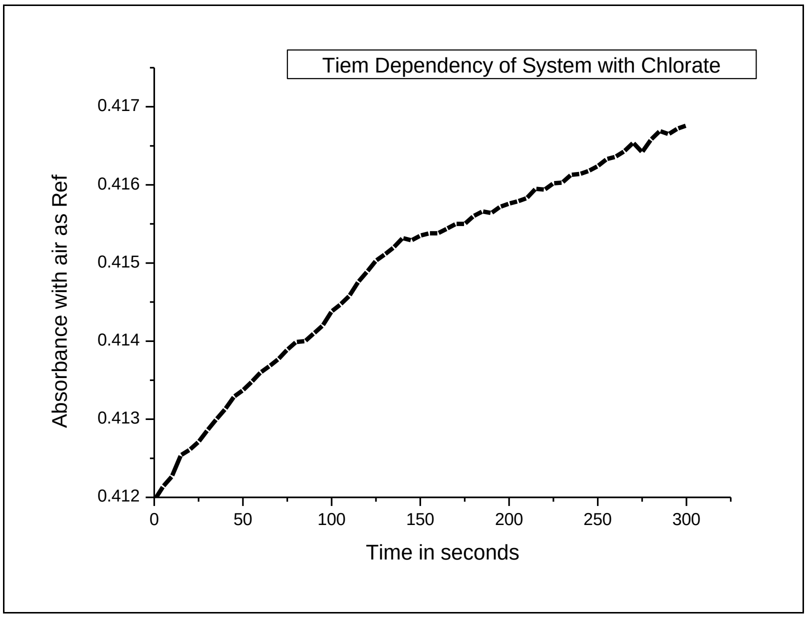


Figure 4.36: Pre- irradiation time dependence study of chlorate added uncatalysed system

Even at higher pH (using borax as buffer) chlorate was ineffective as antioxidant for the iodine based system and the absorbance value were found to increase steadily. Chlorate (1 mol/m^3) along with borax (to maintain alkalinity) also proved to be ineffective in improving stability (Figure 4.37).

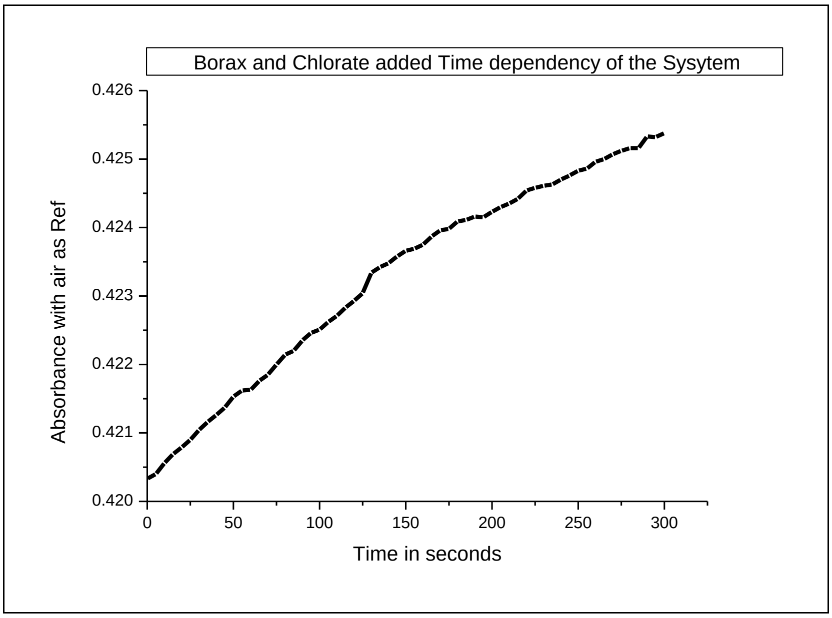


Figure 4.37: Pre- irradiation time dependence study of chlorate and borax added uncatalysed system

Nitrate ions act antioxidants for various systems as they compete for oxidation reactions, potassium nitrate (1 mol/m^3) was added along with borax to the system but absorbance of control solutions before continued to increase with time. Thus nitrate was also unable to hinder the oxidation reaction (Figure 4.38)

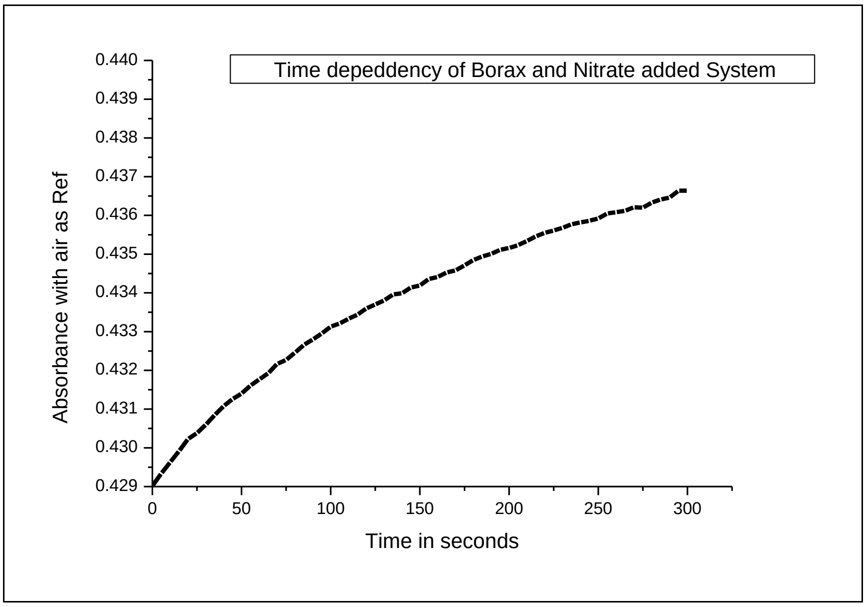


Figure 4.38: Pre- irradiation time dependence study of borax and nitrate added uncatalysed system

Sodium hydroxide (2 mol/m^3) was added to borax catalysed system (buffer having pH 10) in an attempt to keep the pH unaffected by iodination reaction occurring in solution before irradiation. Although it improved the absorbance measurements the rise in absorbance values continued (Figure 4.39).

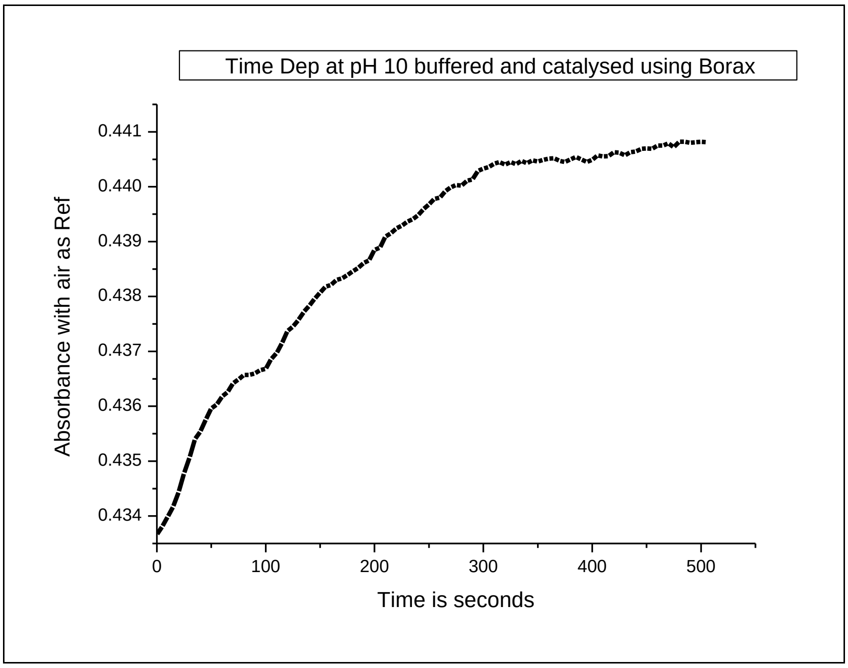


Figure 4.39: Pre- irradiation time dependence study of borax at pH 10 uncatalysed system

Antioxidants such as sulphite, bisulphate, thiosulphite are known to decrease iodide oxidation. They are widely used to stabilize and store radioiodide solution (Luckett and Stotler 1980). They were added in solution to improve the pre-irradiation stability of system by lowering the oxidation of iodide. Antioxidants were found to lower the rate of iodide oxidation to a considerable degree as observed experimentally.

The use of bisulphite, thiosulphite and sulphite for converting halogens dissolved in aqueous solutions to their respective halides. In radiopharmaceutical applications, radioiodine is supplied by stabilizing it with thiosulphite and sulphite in alkaline medium. They were tried in various combinations with borax and sodium hydroxide. 1 mol/m3 of antioxidant was added either alone or in combination with 1 mol/m^3 NaOH or with 5 mol/m^3 borax.

Solutions with sulphite were found to be more stable before irradiation as compared to solutions without sulphite. This was also found to be true for sulphite solutions additionally containing sodium hydroxide. Bisulphite, thiosulphite show similar effect however, borax was ineffective when added along with these antioxidants.

The reactions of thiosulphite with iodine and triiodide to form iodine are given

$$2\,S_2O_3^{2-} + I_2 \rightleftharpoons S_4O_6^{2-} + 2\,I^-$$

$$2\,S_2O_3^{2-} + I_3^- \rightleftharpoons S_4O_6^{2-} + 3\,I^-$$

Since iodine is getting converted to iodide the activity of iodine in solution is greatly reduced. In alkaline medium, forward reactions are favoured. (Figure 4.40 through Figure 4.46) present results of the experiments conducted.

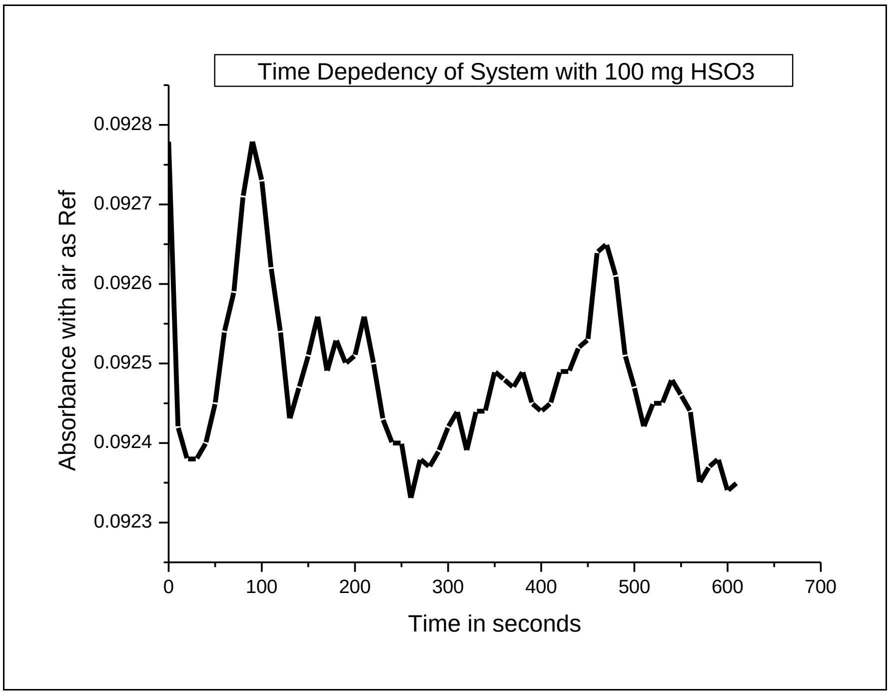


Figure 4.40: Pre- irradiation time dependence study of borax at pH 10 uncatalysed system

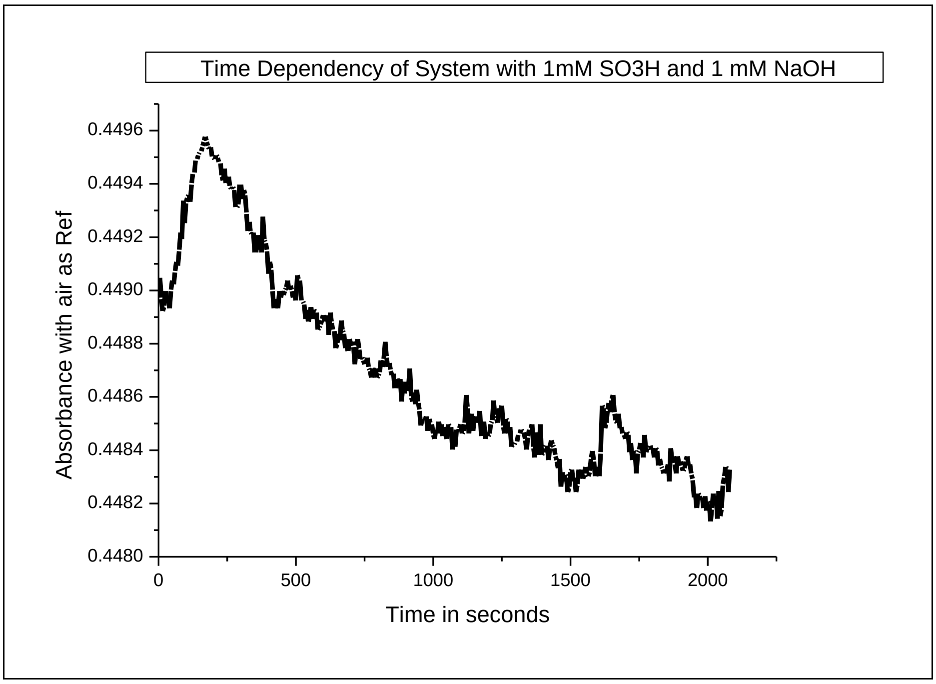


Figure 4.41: Pre- irradiation time dependence study of alkaline sulphite pH 9 added uncatalysed system

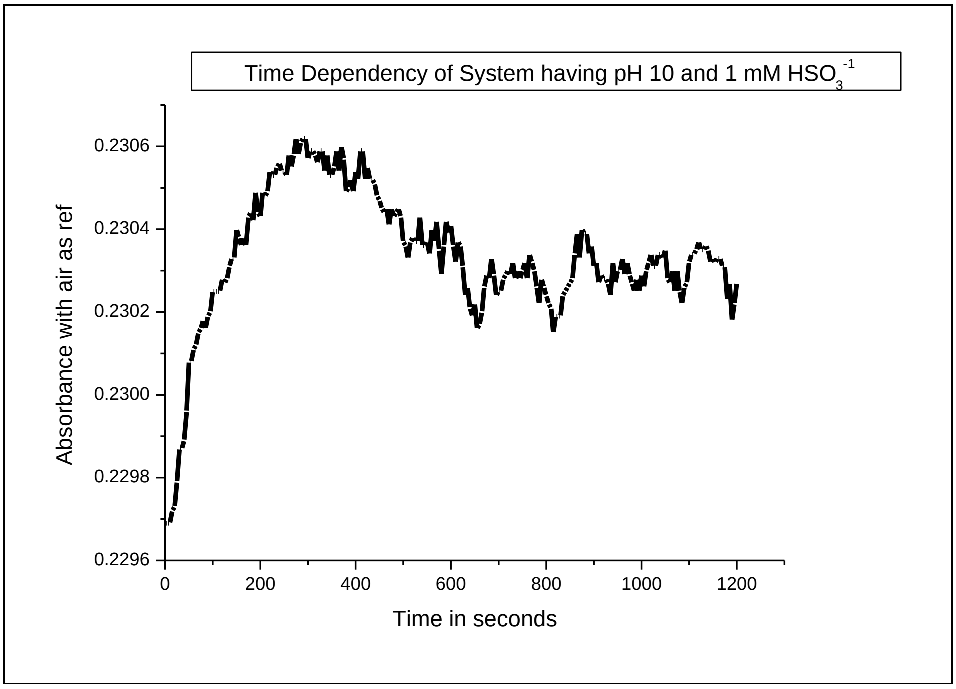


Figure 4.42: Pre- irradiation time dependence study of alkaline sulphite with pH10 in uncatalysed system

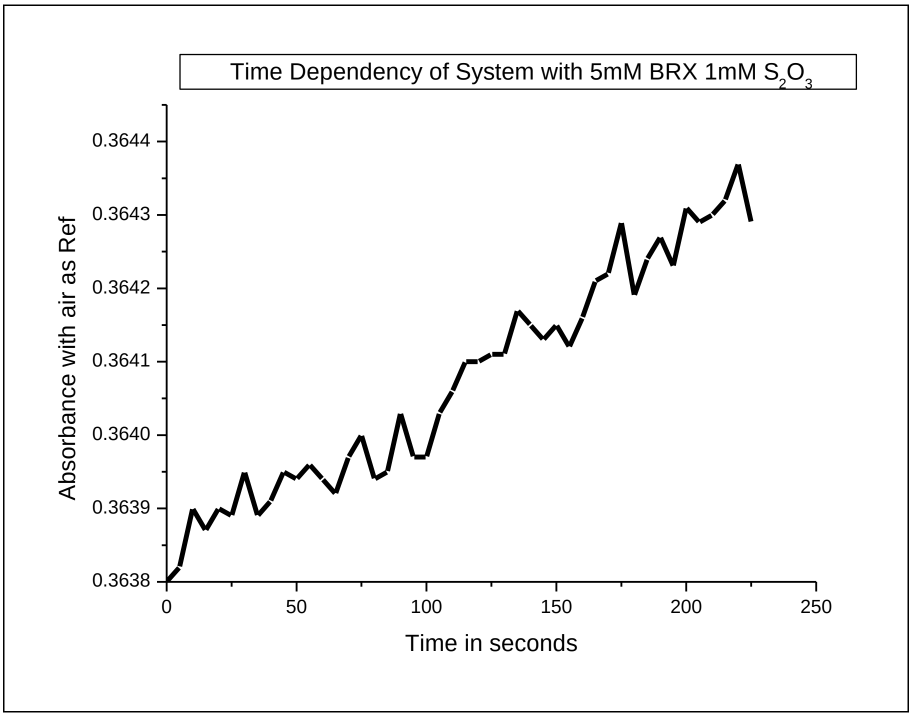


Figure 4.43: Pre- irradiation time dependence study of borax and thiosulphite added uncatalysed system

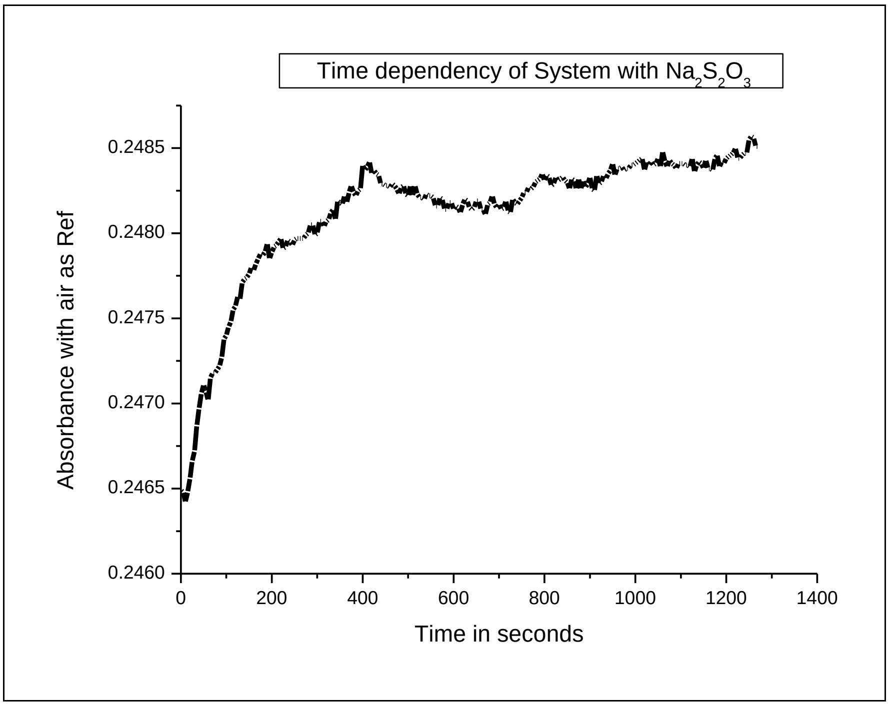


Figure 4.44: Pre- irradiation time dependence study of NaOH (2 mol/m^3) thiosulphite added uncatalysed system having pH 10

Although use of antioxidants improves the pre- irradiation stability of the systems, the radiation dose response is totally changed. The minimum detectable dose is increased from 200 Gy to 2 kGy, probably due to conversion of radiolytically generated iodine to iodide ion thus lowering its availability in solution. The increase in absorbance with dose is abrupt and non-reproducible. Other antioxidants tried show similar effects. To conclude, addition of chemical antioxidants do reduce the oxidation of iodine but at the cost of drastic change to dose absorbance relation. 100 mg sulphite was added in 100 ml of dosimeter solution as per standard protocol used for radioiodine solutions and the pH was maintained at 10. Although the absorbance readings of control solutions were very low, after irradiation the solution shows a continuous rise in absorbance.

As all efforts to control the pre irradiation absorbance turned futile, the dosimeter solutions were prepared fresh and all stock solutions kept refrigerated at all times to reduce the atmospheric oxidation of iodides.

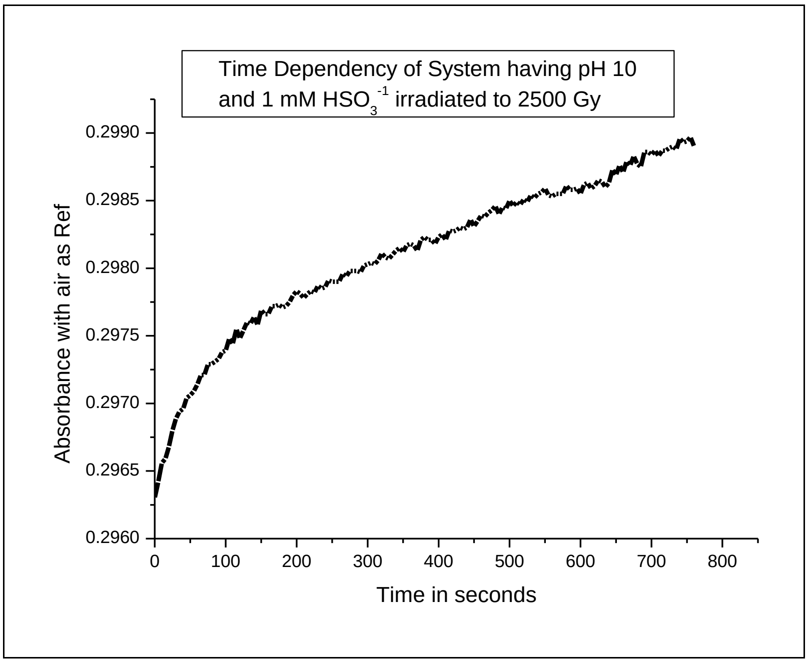


Figure 4.45: Post- irradiation time dependence study of alkaline sulphite added uncatalysed system having pH 10 after 2500 Gy dose

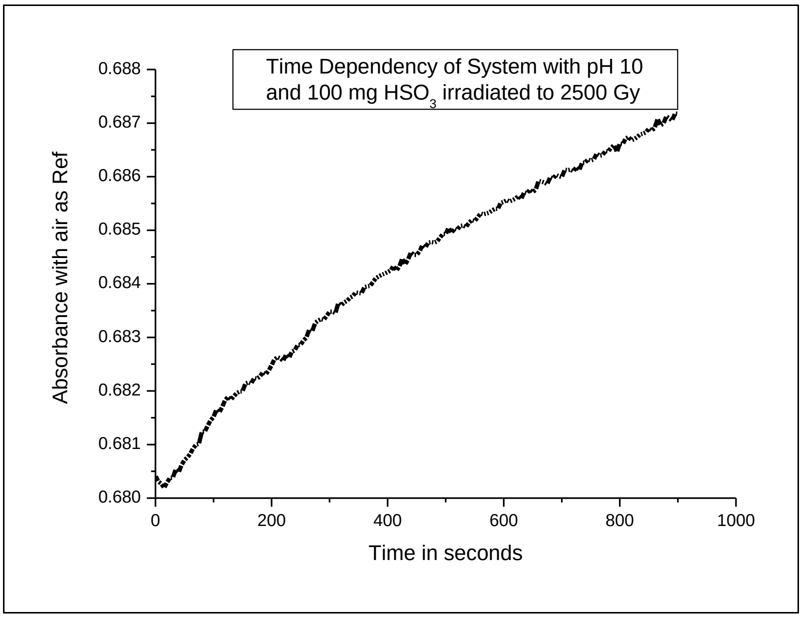


Figure 4.46: Post- irradiation time dependence study of alkaline sulphite (100 mg) added uncatalysed system having pH 10 after 2500 Gy dose

Post Irradiation Stability

It was observed that after irradiation, absorbance values increase rapidly with time. The absorbance value then begin to decrease followed by a continual increase. The increase in absorbance may be due to slow reactions getting complete or other unexplained radiation chemical reactions (Figure 4.47, Figure 4.48, and Figure 4.49).

Some popular dosimeter systems like radiochromic film FWT60 suggest use of short (5 minutes) heating cycles for films at temperature of 65°C to improve post irradiation stability of their system.

The reactions involving iodine formation and their interactions are fast and get completed very quickly. Bicarbonate concentration was increased in an attempt to complete iodination reactions as bicarbonate is driving molecule for iodination of fluorescein. Although it 2.5 mol/m^3concentration is optimally sufficient for iodination reactions. Higher concentration of bicarbonate will hasten the reaction and the post irradiation rise in absorbance can be reduced.

Bicarbonate concentration was increased by four times i.e. 10 mol/m^3 and it was proved beyond doubt that, at higher concentration post irradiation stability was greatly improved as shown in Figure 4.50 and Figure 4.51. At 20 mol/m^3 bicarbonate (8 times) the post irradiation stability was excellent due to completion of the reaction. From the study we conclude that 10 mol/m^3 as optimum bicarbonate concentration. Also as it is clear from the observations, it is therefore suggested that all absorbance measurements be performed at least 10 minutes after irradiation; it is also advisable to complete the measurements within 120 minutes, to minimize the error due to variation in absorbance with time.

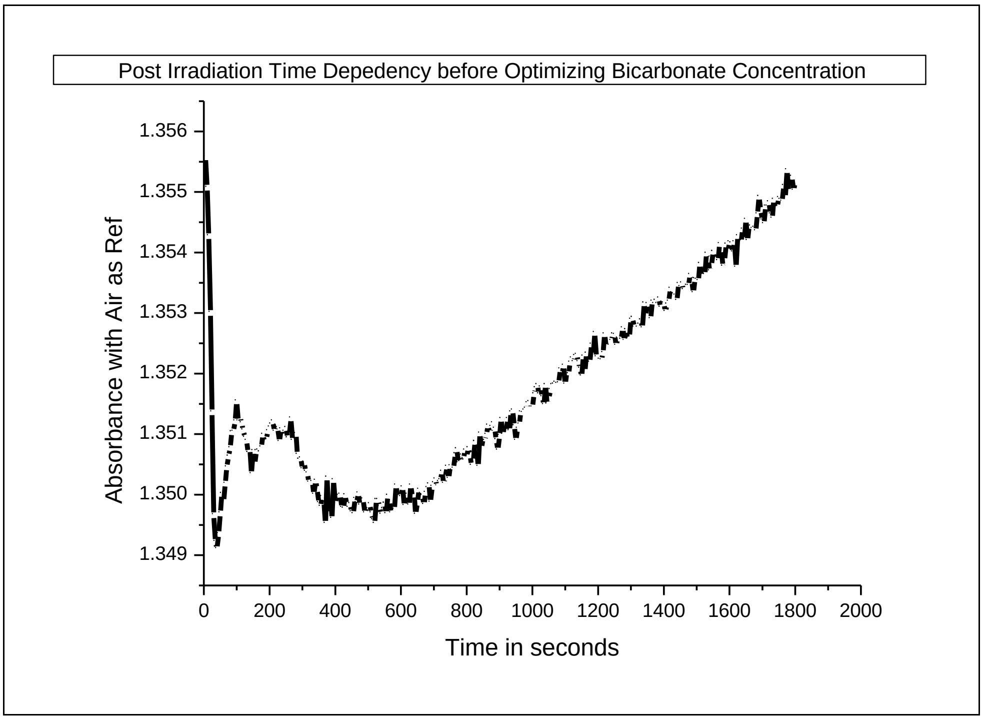


Figure 4.47 Post- irradiation time dependence of uncatalysed system done immediately after irradiation

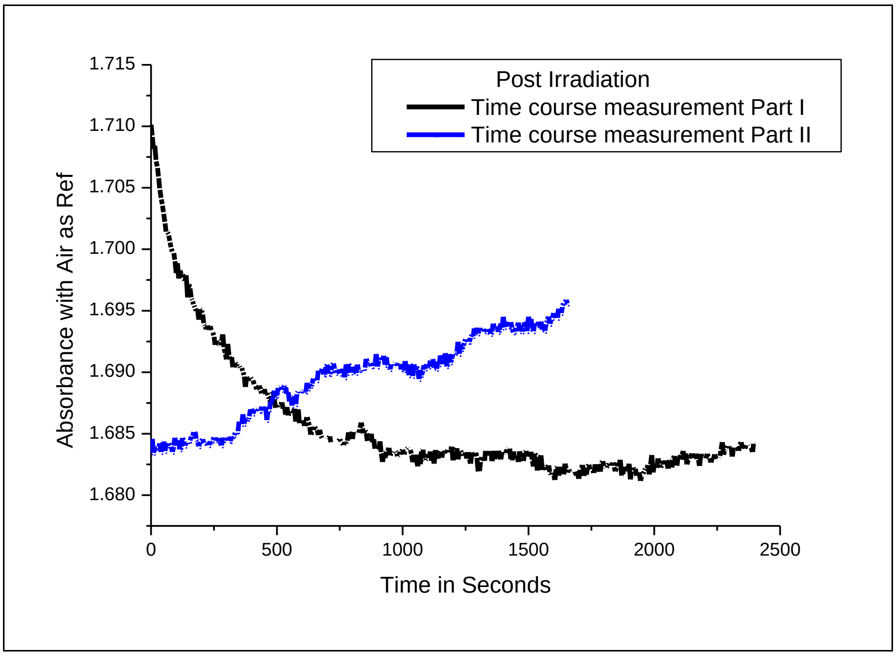


Figure 4.48 Post- irradiation time dependence of uncatalysed system done 15 minutes after irradiation to complete slow reactions

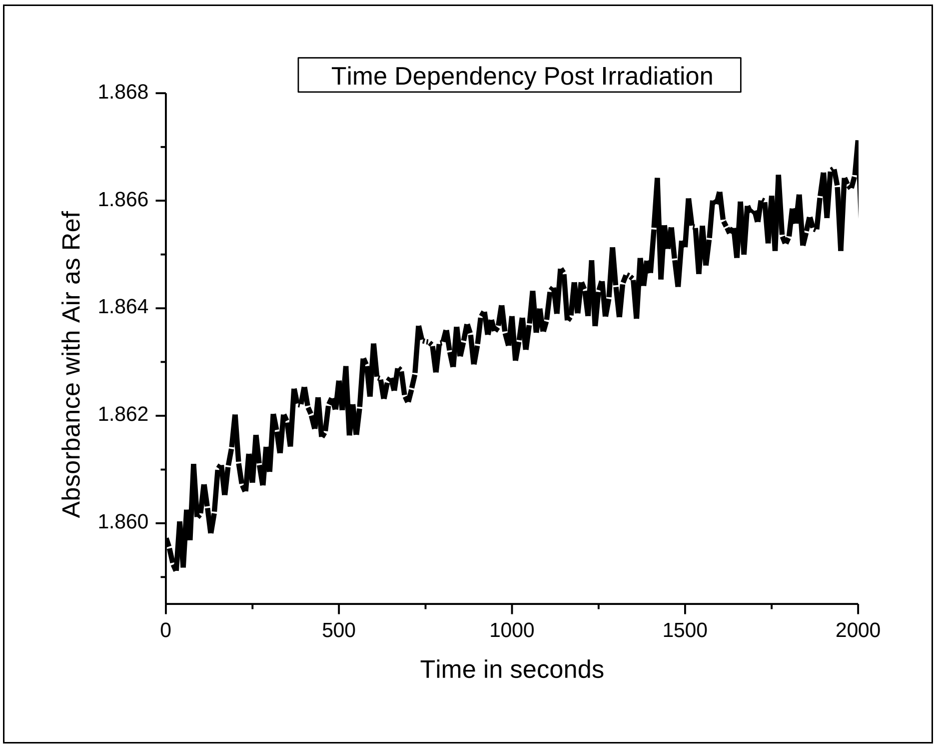


Figure 4.49: Post- irradiation time dependence of uncatalysed system continued after a gap of 60 min as continuation of earlier graph

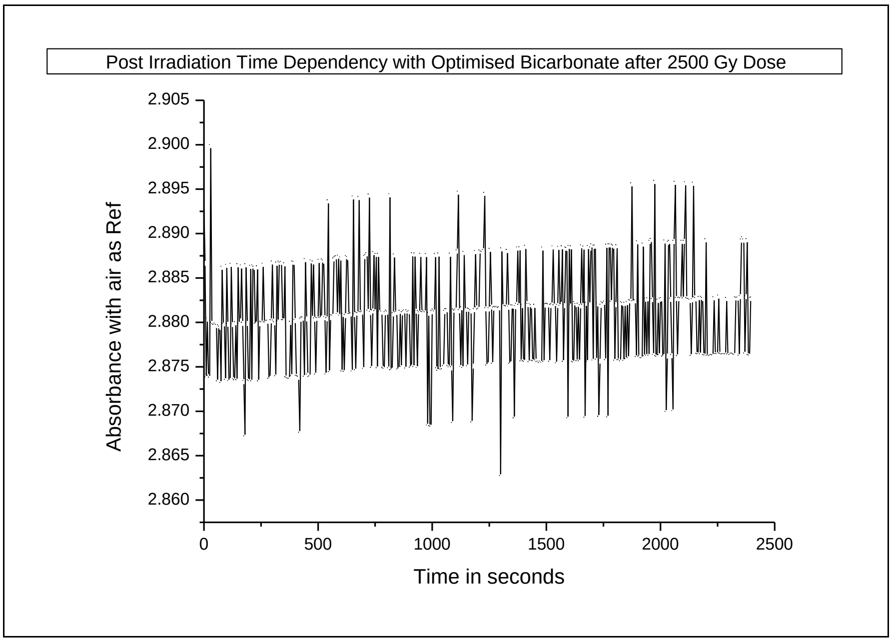


Figure 4.50: Post irradiation stability with optimized bicarbonate concentration irradiated to a dose of 2500 Gy

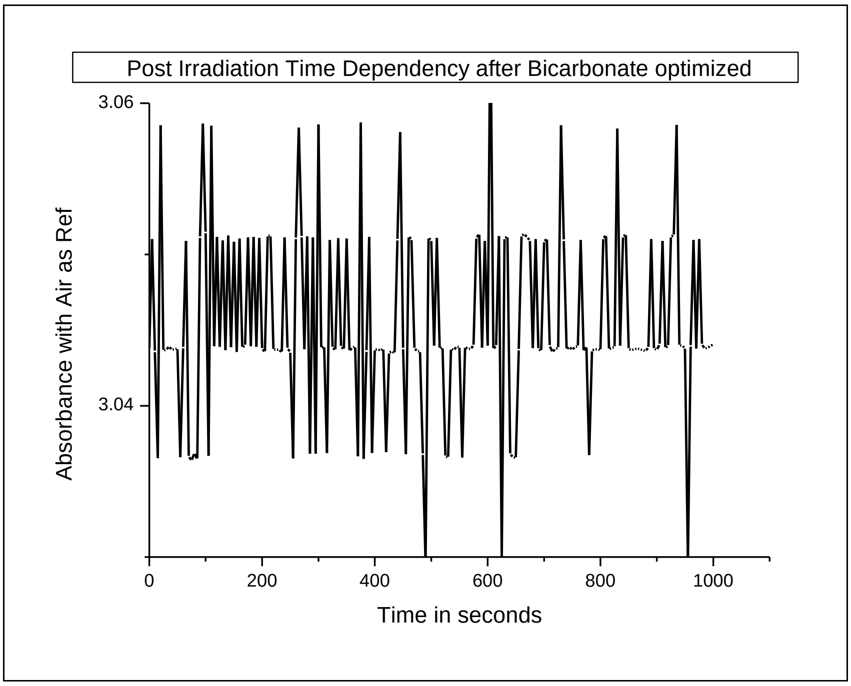


Figure 4.51: Post irradiation stability with optimized bicarbonate concentration irradiated to a dose of 2500 Gy as continuation of earlier graph after gap of 60 minutes

Any change in composition results in alteration of dose absorption relation. After increasing bicarbonate concentration, new dose absorbance relation was established.

For radiochromic systems, a researcher has suggested use of two wavelengths for evaluation of dosimeters in two different dose ranges (Xinghong, et al. 1988). In the iodine based system developed, the measurement wavelength used was 525 nm, so as to increase the dose sensitivity of the system.

Few changes were made in an attempt to improve the system. Iodide solution were stabilized by adding sodium hydroxide to stock solutions (1mol/m^3 NaOH concentration) before using it for preparing solutions. Borax concentration of 5mol/m^{3}is maintained in the solution to maintain the pH around 9.5.As the saturation dose wavelength of maximum absorption is 542 nm, 540 nm was chosen for analysis. At 540 nm the pre irradiation variation in absorbance values was found to reduce, thus improving the stability of the system. Even after 20 days of storage at refrigerated conditions the solutions showed good pre-irradiation stability. The change in parameters results in improved pre-irradiation stability and dose absorbance relation, thus improving the overall performance of the dosimeter system. The above system is the final optimized system used as radiochromic dosimeter.

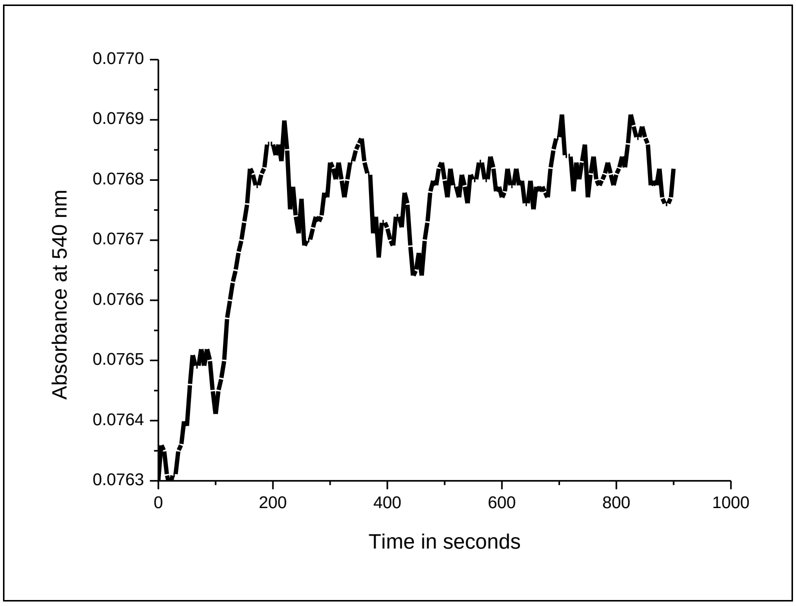


Figure 4.52: Pre-irradiation time dependence of freshly prepared solution

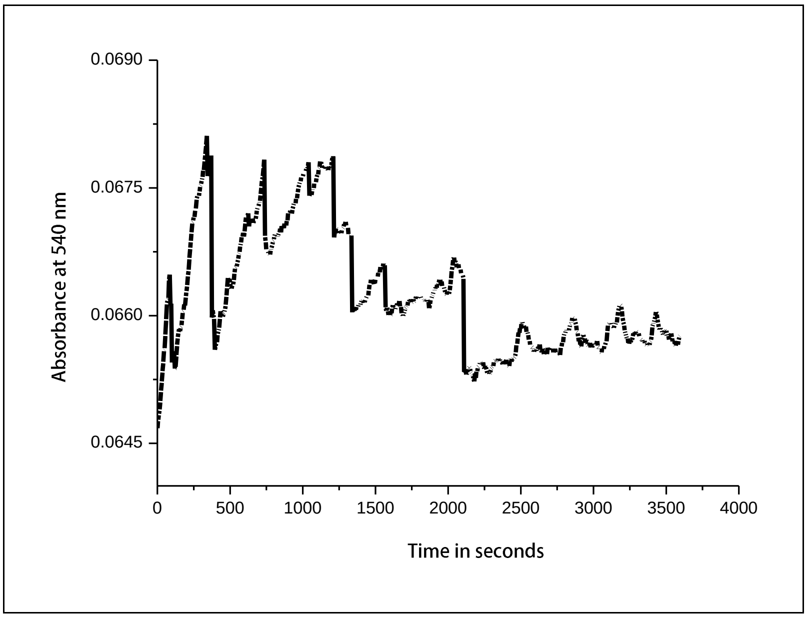


Figure 4.53: Pre-irradiation time dependence for 20 days old solution (refrigerated)

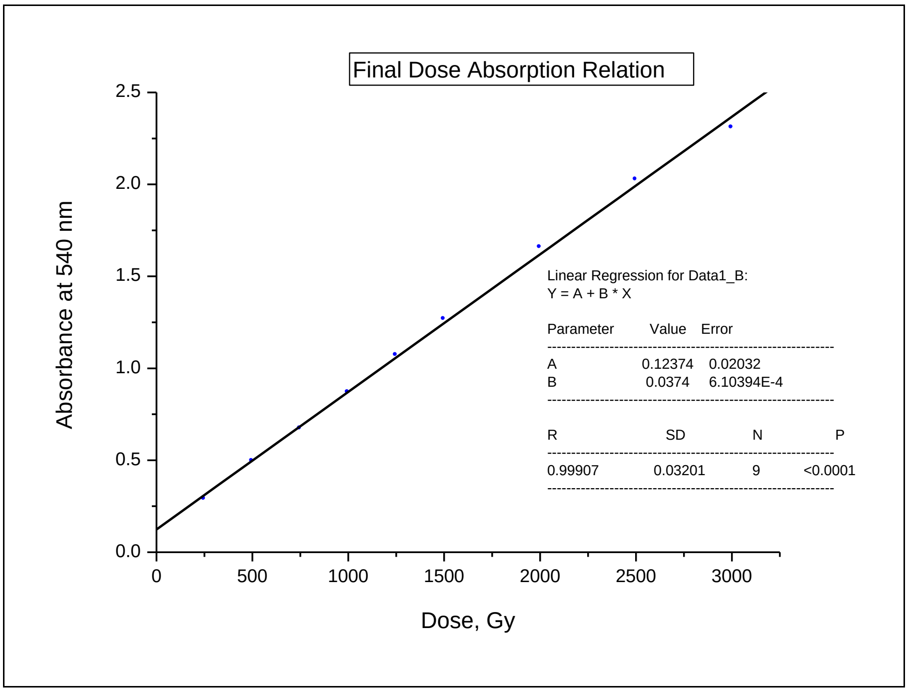


Figure 4.54: Final Dose-Absorption Relation for optimised radiochromic dosimetry system

The final dose absorbance curve is linear fit as shown in Figure 4.54. Two different dose rates 10 Gy/min and 40 Gy/min were used to study the effect of dose rate on the system; however, no significant effect of dose rate was observed. Preliminary, dose fractionation study suggests negligible effect of dose fractionation under the experimental conditions.

The solution after preparation should be kept between 5-10°C (refrigerated conditions).The study suggest that the developed radiochromic dosimetry systemis extremely simple to prepare, made from easily available and relatively nontoxic chemicals. Figure 4.55 shows the actual photograph.

Table 4.8: Results of reproducibility study conducted for optimised radiochromic system

Dose, Gy	Absorbance	Dose, Gy	Absorbance
200	0.5371	1965	2.0156
200	0.5312	1965	2.0457
200	0.5417	1965	2.0576
200	0.5337	1965	2.088
200	0.5192	1965	2.0457
200	0.5302	1965	2.0605
200	0.5441	1965	2.019
200	0.5416	1965	2.0413
200	0.5302	1965	2.0642
200	0.5326	1965	2.0717
Percentage standard deviation	0.74		2.24

The study indicates good reproducibility of the system in the dose range of 200-2000 Gy. Reproducibility experiments were done on same day to avoid any error due to increase in absorbance of unirradiated control solutions. This test is an important requirement for system to establish as dosimeter (Woods and Pikaev 1994).Table 4.8indicates the reproducibility of the system.

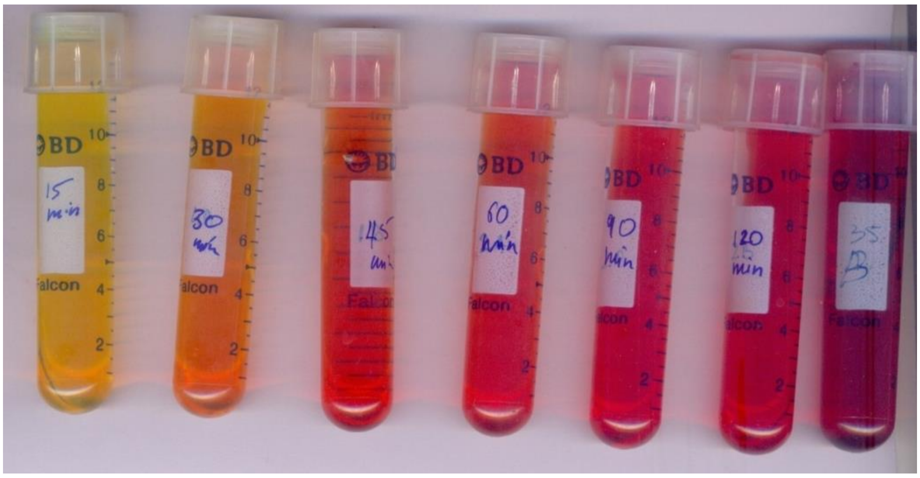


Figure 4.55: Colour development with dose in radiochromic dosimeter

4.4.4 **Conclusions**

The study suggests that radiation chemical synthesis of erythrosine can be utilized as radiochromic dosimeter after finalizing the reagent concentrations. The system is extremely simple to prepare, made from relatively nontoxic chemicals that are easily available.

The radiochromic dosimeter developed has no special requirement such as glass container for filling or triple distilled water for solution preparation as required by currently available systems. Solutions are made using single distilled water and irradiation can be performed in polymer containers (polypropylene). The cost of dosimeter solution will be less than 5 rupees (per 5 ml) for single dose measurement at lab scale. All absorbance measurements can be done using standard spectrophotometer or colorimeter using standard glass or Perspex cuvettes, although for accurate dose measurements use of calibrated spectrophotometer is recommended. All irradiations and measurements were carried out at room temperature. Refrigerated storage of solutions prepared is highly recommended. User is advised to use fresh prepare solutions for better reproducibility. It is also advised to evaluate dose absorbance relation at user location under controlled conditions before evaluating and reporting doses.

Chapter 5 Development of Radiation Indicator Gels and Films for Radiation Processing

5.1 Introduction

Sterilization is a validated process used to render a product free from viable microorganisms and is described by an exponential function. Presence of microorganisms on the individual item can be expressed in terms of probability. While the probability may be reduced to a very low number, it can never be reduced to zero. The probability can be expressed as a Sterility Assurance Level (SAL); it means probability of a viable microorganism being present on the product unit after sterilization.

There exist several chemical and physical methods of sterilization. In case of radiation sterilization, inactivation of microorganisms occurs either through direct ionization of a vital cellular molecule (DNA, key enzyme, etc.) or indirectly through the reaction of the free radicals produced in the cellular fluid.

For radiation sterilization

- radioactive isotopes (gamma rays from Co-60 or rarely, from Cs-137),
- particle accelerators (high-energy electrons) are used.

The choice of radiation source for a particular application depends on such requirements as product configuration, minimum dose, max/min dose ratio, economical factors, etc.

Radiation Sterilization is important application of radioisotopes towards health care offered on a commercial basis to the Indian medical industry. The ability of gamma radiation to eliminate micro-organisms is effectively made use of in radiation sterilization of various medical products such as disposable syringes, surgical sutures, cotton dressing, drugs and related products etc. The advantage over conventional techniques is that the sterilization is effected in the final packing so that the product remains sterile up to the point of use.

Moreover, as it is a cold process, heat sensitive materials like plastics used in medical products are not adversely affected. Over a million radiation sterilized midwifery kits and delivery packs, to be used in rural areas for preventing infection of mothers and helping to minimize infant mortality rate, have been distributed through rural health programs funded by WHO and this has decreased infant mortality rate in the areas where these kits were supplied.

Gamma Radiation Sterilization

Almost all medical products are commonly sterilized by gamma radiation. An indicative list of these products is given below:

- **Surgical Disposables :** Surgical Sutures, Bandages, Dressings, Gauge pads, Nappies, Delivery Kits etc., which are made of Cotton Wool and Gauge.
- **Metallic Products:** Surgical Blades, Needles, Implants, Aluminum Caps, Containers etc.
- **Plastic And Rubber Items:** Petri-dish, Centrifuge Tube, Blood Collection Sets, Scalp Vein Sets, Shunt Valves, Rubber Gloves, Contraceptive Devices, Gowns, Wraps Covers, Sheets, etc.
- **Pharmaceuticals:** Silver Sulphadiazene Cream, Gelatin Capsule, Bentonite Charcoal, Ergot Powder, Absorbable gelatin, Ophthalmic preparations in paraffin base and oil base, Skin Ointment in Polyethylene glycol base.

Advantage of radiation sterilization

- Unlike heat sterilization or steam sterilization, Gamma ray sterilization does not significantly increase the temperature of the products and therefore can be used to sterilize safely even the heat sensitive materials as well as materials in frozen condition.

- Unlike Ethylene oxide sterilization, gamma sterilization does not leave any harmful residue. In products exposed to gamma rays from Cobalt-60 source at the normally used dose level, there is no danger of radioactivity or toxicity. Radiation processed products does not become radioactive- just as our body do not start emitting X -rays after being X-rayed.
- Gamma sterilization is performed after packaging of the products in the final containers and does not involve any aseptic handling. Product sterility is retained indefinitely, as long as the packaging is intact
- Sterilization of products of any shape can be achieved due to the high penetration ability of gamma rays.
- Gamma ray sterilization is non-polluting, environment friendly process, and since it is a continuous process, the results are more uniform than gas or high temperature sterilization, which are essentially batch processes.

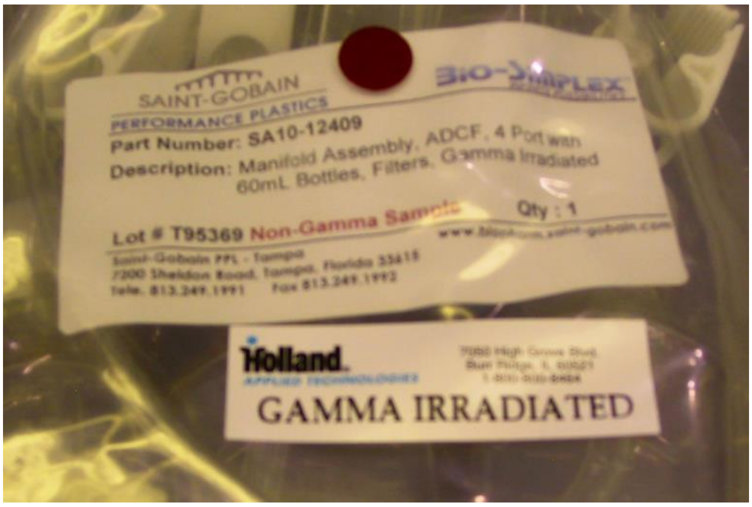


Figure 5.1: Labeling of products with radiation indicator (red dot)

Various products have been approved by FDA Maharashtra for Radiation Sterilization at ISOMED, Mumbai which are listed as below.

Products approved for routine radiation sterilization:

- Bandages - crape, cotton crape, gauze
- Cotton - buds, pads and swab
- Dressings- paraffin gauze, shell and finger
- Gauze pads
- Kits- maternity, minor surgery & vasectomy
- Absorbable gelatin sponge
- Opthalmic ointments in paraffin base atropine sulphate, chloramphenicol, gentamycin sulphate, tetracycline
- Skin ointments in PEG base - neomycin sulphate hydrocortisone acetate alpha chymotrypsin
- Sutures - Catgut, linen, polyester and silk
- Herbal and Ayurvedic products
- Contraceptives, Intrauterine devices
- Perfusion Sets
- Drugs, Pharmaceuticals and Veterinary drugs.
- Orthopaedic Products Bone grafts, Bone Implants, Bipolar, Nails (Tibia and Femur), Orthopaedic implants, A.M. Prosthesis

Productsapproved for Export Purpose only:

- Belladonna dry extract
- Chlorotetracycline
- Ergot powder
- Hydrocortisone neomycin
- Rawolfia serpentine

Products which do not require FDA approval:

- Containers and Closures: Bottles, Bungs, Caps, Droppers, Petridish, Plugs, Spike Caps, Empty kajal barrels, Empty aluminium tubes
- Medical Accessories: Aprons, Drapes, Gloves, Mayo trolley cover
- Surgical Products: Blades, Gloves, Implants, Instruments and Tools

Table 5.1 Commissioned Radiation Processing Plants in Private Sector

1.	Organic Green Foods Ltd., Kolkata	West Bengal	Food, Packaging & Medical Products
2.	A.V. Processors Pvt. Ltd., Mumbai.	Maharashtra	Food & Medical Products
3.	Universal Medicap Ltd., Vadodara	Gujarat	Food & Medical Products
4.	Microtrol, Bangalore	Karnataka	Food & Medical Products
5.	Agrosurg Irradiators, Mumbai	Maharashtra	Food, Packaging & Medical Products
6.	Gamma Agro Medical Processing, Hyderabad.	Andhra Pradesh	Food & Medical Products
7.	Jhunsons Chemicals Pvt Ltd., New Delhi	Delhi	Agro, Medical & Packaging Products
8.	Innova Agri Bio Park Ltd., Malur	Karnataka	Food &Medical Products
9.	Hindustan Agro Co-Op Society Ltd., Rahuri,	Maharashtra	Onion & Other Agricultural Produces
10.	NIPRO India Corporation Pvt. Ltd., Satara	Maharashtra	Medical Products
11.	M/S Impartial Agro Tech (P) Ltd., Unnao, Lucknow	Uttar Pradesh	Food & Medical Products
12.	M/s Gujarat Agro Industries Corpn. Ltd, Bavla, Ahmedabad,	Gujarat	Food Products

The increased importance of the use of high energy radiation both in the field of medicine and in the sterilization of food products or other consumer goods, has made it increasingly desirable to provide simple and reliable means for indicating whether or not the materials exposed to high energy radiations have been properly exposed.

For commercial application, a simple indicator is required to assure that all exposed materials can be readily recognized post irradiation treatment.

The present work relates to method for radiation indicator development in gel and film form. They find application as high energy radiation indicator. In case of high energy radiation such as radiations having an energy of one hundred thousand electron volts or higher, such as X-rays, alpha, beta, and gamma rays, high energy electron beams, etc., the effect of the radiation is practically independent of the chemical structure of the substances exposed and is rather dependent on the mass of the absorbing material, the absorption occurring throughout its mass. In general, such high energy irradiations bring about excitation of the exposed molecules and cause ionization. Thus, in the case of water, hydroxyl radicals and hydrogen atoms are formed ultimately with the intermediate formation of various other products. Accordingly, in the case of systems containing water, generally oxidation and reduction processes can occur; however, some side reactions can be caused by unstable ions, activated molecules, or free radicals. In the past, a number of indicators for such high energy irradiations have been suggested. To mention a few, aqueous solutions of methylene blue or methylene blue solutions in agar gels and resazurine in agar gels. While such systems have been found of value and practical for research investigations, they do not lend themselves readily for commercial and other practical applications. Indicator systems of the type mentioned undergo a change from their colored state to uncoloured compounds on irradiation with high energy radiation. The decolourisation effect is not restricted to ionizing radiation and bleaching due to solar exposure can give erroneous results.

Radiation indicators provide visual indication of whether or not a product has been adequately exposed to ionizing radiation, aiding in the segregation of product for inventory control. Although they provide quality control check, proper dosimetry should be accompanied for validation of the process. Presently, for use in gamma, electron beam and X-ray sterilization applications, radiation indicator labels are self-adhering type; that are permanently fixed to any package or box surface. Size of radiation indicator varies according to application, 13 mm diameters being the most common size. Some indicator manufacturers claim (ANSI/AAMI/ISO1140 2014)and (ASTM 51540 2004) compliance. In India, presently radiation sterilization indicators are imported from western countries. Some locally manufactured labels are available, however post irradiation instability and poor availability limit their use. Most common color change with gamma radiation exposure begins with yellow for unirradiated to light range at 10kGy; burnt orange at 15kGy and at 25kGy maximum color change is achieved at brick red. In addition to these, more radiation sensitive indicators are available for specific purposes.

Highly dose sensitive compositions are used in personal monitoring applications in case of nuclear and radiological accidents for estimation of approximate dose.

5.2 Development of Radiation Indicator Gels

This section discusses development of radiation processing dose indicators gels. Many gel formulations have been proposed earlier for radiobiology and radiotherapy applications. Ferrous Xylenol Orange based gels being the most commonly used by radiobiologists. It is the most often used radiochromic gel because of its high dose sensitivity. A drawback is the diffusion of dose patterns due to which the evaluation of dose response should be done shortly after irradiation (Šolc, Sochor and Kozubíkov 2015). Sucrose and other reagents were tried by some researchers to sensitize the dose response (Juarez-Calderon, Negron-Mendoza and Ramos-Bernal 2014).

Many other sensitive systems independent of ferrous have been studied to reduce the error caused due to drift of ions post irradiation. Radio-fluorogenic gel (RFG) developed to image the ionization track of an 80 MeV proton pencil beam (Warman, et al. 2013). Some authors have suggested use of Sulfosalicyclic acid-Ferrous-PVA hydrogel for use as 3D dosimeter (Yang, et al. 2015)

Use of Leuco Crystal Voilet gel with an optical CBCT scanner for radiotherapy dosimetry has also been investigated for use in radiobiology applications (Ebenezer and Ravindran 2013).

Above mentioned gels are used extensively for dosimetry in low dose range. The present work deals with development of the gel based radiation indicators based on radiochromic dosimeter developed and discussed in earlier sections.Conversion of radiochromic dosimeter into gel was tried as a non spillable version of radiation indicator. The radiochromic indicator gel is extremely easy to make and requires commonly available chemicals. Colour change produced is irreversible, stable and highly contrasting. Additionally, water based gels have negligible temperature effect due to high water content and dose absorbed is close to that received by product. Iodination of fluorescein is specific to high energy radiation and irreversible, making it convenient to be used as a radiation indicator. The inexpensive indicator can be used for dose assurance in radiation processing applications. As the colour developed is stable for more than a year, gel based indicators can be used for keeping record of irradiation process. Moreover, the dye, fluorescein is simple and relatively nontoxic to general biota (V. Miller 2000) thus can be handled easily.

5.2.1 **Principle**

Radiochromic dosimeter was developed and discussed in section 4.4 where borax was found to catalyze the radichromic solution system.

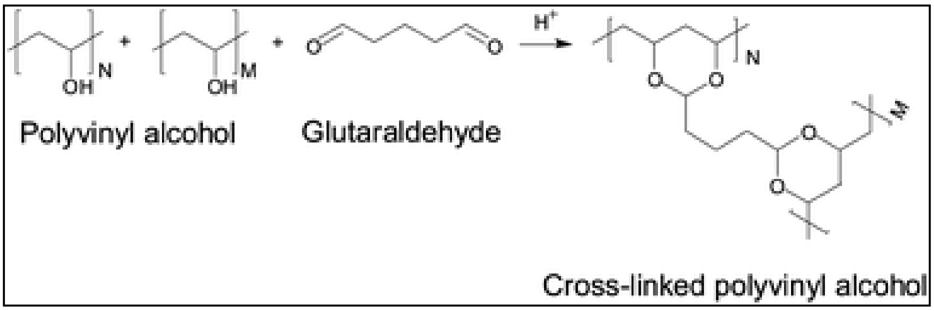


Figure 5.2: Acid catalysed cross linking

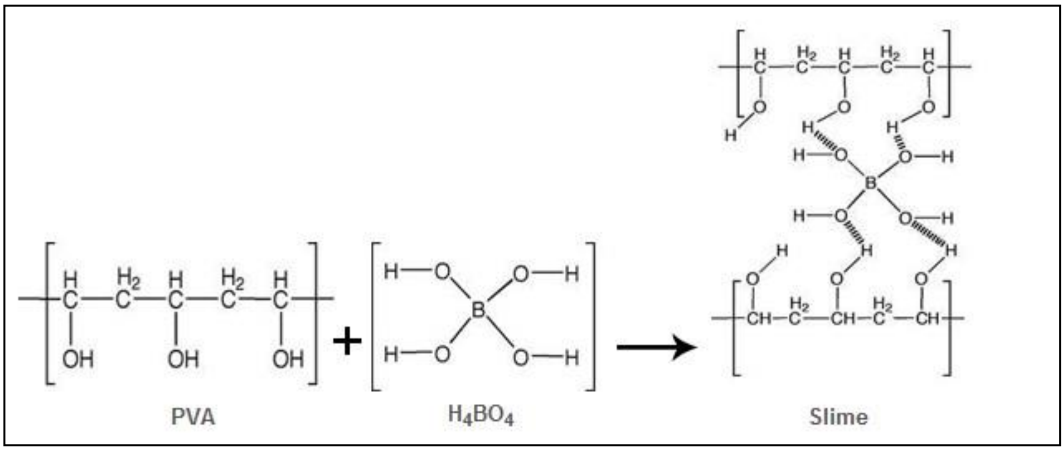


Figure 5.3: Alkali catalysed cross linking

Polyvinyl alcohol can be cross linked by glutaraldehyde under acidic conditions (Figure 5.2) and borax under alkaline conditions (Figure 5.3) (Spoljaric, et al. 2014)to form slime/gel. Since the medium is alkaline and catalysed by borax, polyvinyl alcohol was found to be the best alternative for gel formulation. The radiochromic solution forms gel that can be packed into small plastic pouches or centrifuge tubes and kept alongside commodity to be radiation processed.

5.2.2 Reagents and Preparation

For preparation of radiation processing indicator gel, polyvinyl alcohol (Mw 89,000-98,000, 99+% hydrolyzed) of Sigma Aldrich make was used.Initial experiments were performed to fix concentration of polyvinyl alcohol to be used. Some papers suggest 10 % PVA solutions for making films (Beshir 2013); (Ogawa, Nishikawa and Nishim 1987). During experiments it was found that 5 % solutions gave the optimum viscosity. Beyond 7 % the viscosity becomes too high and the solution becomes very thick and resists flow. Lower concentration solutions (< 3%) tend to behave more like true solutions rather than gels thus defying the very cause of gel formation. Viscosity of the solutions was found to increase upon receiving radiation dose, hence to adjust for this post irradiation viscosity change, 5% PVA concentration is chosen to be optimum.

Polyvinyl alcohol stock solutions were made by heating polyvinyl alcohol in single distilled water at 70 °Celsius for 4 hours with continuous stirring. The prepared solution was cooled to room temperature and kept unstirred for next 6-8 hours. The clear supernatant liquid is carefully decanted after skimming the film formed on surface. The obtained liquid is used in preparation of the gels without any further treatment.

Two main factors affecting gel formation:

i. pH: As alkalinity increases the cross linking increases proportionally till a point of saturation.
ii. Concentration of borax: Cross linking increases with the concentration of borax.

5.2.2.1 **Determination of optimum composition**

Reagent concentrations of radiochromic dosimeter were taken for preparing gels.To prepare 100 ml of gel, 50 ml radiation processing indicator solution with double concentration (double concentration solution consists of 20 mol/m^3 of iodide and 10 mol/m^3 iodate, fluorescein sodium 1 mol/m^3, along with 20 mol/m^3 sodium hydrogen carbonate and 5 mol/m^3 Borax) is added in small batches with slow stirring (fast stirring would make the gel unevenly concentrated and semi-solid). After all the solution was added the solution is stirred in a glass beaker for 10 minutes and kept undisturbed for next 30 minutes. The solution turns into a fluorescent looking gel that is viscous and resistant to flow. The gels are packed in small polythene bags (2 cm X 2 cm) or centrifuge tubes (2.5 ml capacity) for storage. The gels should never be made from stock solutions, as it leads to non-uniform gel formation with separation of liquid component and formation of solid lumps.

5.2.2.2 **Dose Rate and Dose Fractionation Effect**

To study the effect of dose rate on the system, gel samples were irradiated to different doses in GC-900 and GC-1200 having dose rates 10 Gy/min and 40 Gy/min respectively. Dose is fractionated into two equal doses with a gap of 30 minutes and 60 minutes between irradiations to simulate conditions of break down in radiation processing facilities.

Few irradiations were done using e-beam at LINAC located inside BARC.The gel samples were irradiated using dose rates 50 Gy/µsec pulses to dose accumulated dose of 3 kGy. The gels turn red on receiving dose of 3 kGy.

5.2.2.3 **Irradiation and Measurement**

No spectrophotometric absorbance measurements were performed as the gels are highly viscous. Visual observation was noted.

5.2.2.4 **Pre- and Post- Irradiation Stability**

Gels were found to be stable for more than a year, pre and post irradiation. The colour change associated with absorbed dose is reproducible and the gels provide a visual indication of absorbed dose. The non-spillable gels can be stored preferably in refrigerated conditions between 5-10°C.

5.2.3 **Results and Discussions**

Radiation processing indicator gel is developed. The gel is fluorescent yellow in unirradiated form that changes to orange on receiving 5 kGy dose. On further irradiation to dose of 10 kGy the colour of the gel turns deep red.

Fresh radiation indicator gels are stable for more than 12 months. However the gel should preferably be stored in dark conditions between 5 to 25 °C to prevent localisation of dye and reagents and to prevent drying of the gels. Environments with high temperature gradients are not recommended for storage.

Dose rate effect was not observed in the range 10-40 Gy/min. Post irradiation colour change is stable for more than 12 months. The colour developed upon receiving dose is instant and irreversible. Gel is less prone to effects of temperature as compared to radiation indicator solution.

Figure 5.4: Actual photographs of unirradiated and irradiated gel

On sensitization to radiation, the gels can be used for 3D dose mapping by optical CT in radiotherapy applications. Since there is formation of large molecule after irradiation its movement in the gel will be restricted compared to ions and other small molecules presently used (McAuley and Nasr 2013)**;** (Nasr, et al. 2013).

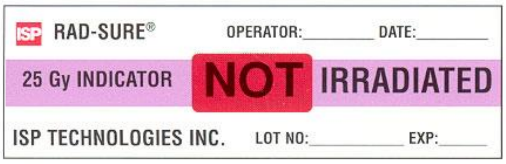
5.2.4 **Conclusions**

Radiation indicator gels developed can be made easily using relatively non-toxic chemicals; the gels can be used as inexpensive replacement to commercially available patented labels. They can be used for record keeping and assurance of radiation processing. The gels can also be used for detection of e-beam radiation processing.

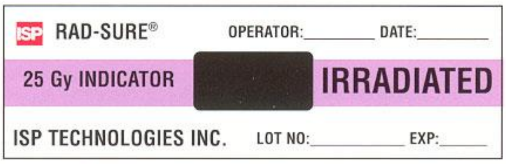
In conclusion radiation indicator gel is developed as a low cost easily available indigenous system to indicate radiation processing. The threshold of dose detected can be changed by adjusting the amount of radiochromic solution added.

5.3 Development of Radiation Processing Indicator Film (Label)

Motivation for the work: Blood irradiation indicators provide positive, visual verification of irradiation. (www.mpbio.com n.d.) When attached to blood products, indicators show whether the blood products have been irradiated or not (Jackson, et al. 2003).

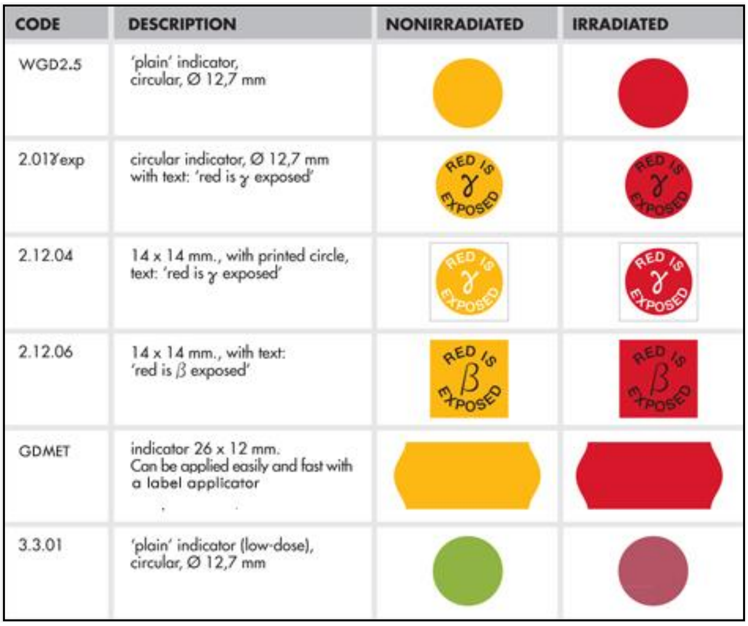


BEFORE IRRADIATION



AFTER IRRADIATION @ 25 Gy

Figure 5.5: Rad-sure radiation indicator



CODE	DESCRIPTION	NONIRRADIATED	IRRADIATED
WGD2.5	'plain' indicator, circular, Ø 12,7 mm	●	●
2.01γexp	circular indicator, Ø 12,7 mm with text: 'red is γ exposed'	RED IS γ EXPOSED	RED IS γ EXPOSED
2.12.04	14 x 14 mm., with printed circle, text: 'red is γ exposed'	RED IS γ EXPOSED	RED IS γ EXPOSED
2.12.06	14 x 14 mm., with text: 'red is β exposed'	RED IS β EXPOSED	RED IS β EXPOSED
GDMET	indicator 26 x 12 mm. Can be applied easily and fast with a label applicator	▬	▬
3.3.01	'plain' indicator (low-dose), circular, Ø 12,7 mm	●	●

Figure 5.6: Commercially available radiation indicators for various purposes

Imported radiation indicators are available to radiation processing facilities at variable costs. At present there are no commercially available systems that are indigenous. Available systems are polyvinyl chloride based patented systems that are imported. For many years different chemical combinations were tried but encouraging results were not obtained.

5.3.1 Films based on Radiochromic solution

5.3.1.1 Principle

Radiation assisted iodination of fluorescein was successfully used as a radiation indicator liquid, radiochromic dosimeter and radiation indicator gel. Polyvinyl alcohol films were cast using radiochromic dosimeter solution hereafter referred to as radiochromic solution, to test its feasibility in solid media for use as radiation indicator label.

5.3.1.2 **Reagents and Preparation**

Polyvinyl alcohol films were made using radiochromic solution without any change in parameters. The concentration of radiochromic dosimeter solution, hereafter referred to as original composition, was used as it is for preparation of radiochromic films.

Films are cast in glass troughs (Petri dish) and peeled off after drying, they are then air dried on the unexposed side.

Films were dried for 2 days in clean atmosphere and cut into 2 sq.cm samples after drying on both sides. Film samples were packed in polythene bags and sealed using heat sealer at STP and about 65 % Relative Humidity.

5.3.1.3 **Experiment Details**

Film samples were irradiated in gamma chambers to different doses to test the feasibility of the process. Films were irradiated to nearly 50 kGy gamma dose in GC-1200. The concentration of original composition in films was doubled in order to increase the overall erythrosine yield. Concentration ratio of iodide iodate to fluorescein was increased (keeping rest composition same) in an attempt to adjust for the loss of iodine produced during irradiation to polyvinyl alcohol and surrounding atmosphere.

As pH plays was found to play a very important role, pH of the solution was changed to 11 and 12 using sodium hydroxide and films were cast from the solution and irradiated.

5.3.1.4 **Results and Discussions**

None of the films prepared using different concentration of reagents displayed any observable colour change. It was observed that when the concentration of original composition in films was raised beyond 2.5 times displayed salting out was observed. The salting out effect causes the films to become translucent.

Glycerine was added to the polyvinyl alcohol (PVA) solution before films are casted as it serves role of plasticiser for PVA (Gager and Sonnichsen 1946)and additionally increases the water content of the films formed. Glycerine was also found to help iodination reactions by absorbing iodine, as observed in experiments conducted for development of radiation indicator.

5.3.1.5 **Conclusions**

The iodide iodate radiochromic solution cast in PVA did not show any colour change. The most probable reason can be low water content in films compared to that in solution and gels. Water content is crucial, as radiolysis products of water lead to iodine formation, also it helps transport of chemical species by serving as a medium and additionally allows iodine to exist in the form of solution as triodide ion.

Films casted using glycerine plasticised PVA become orange after irradiation but the dose required (50 kGy) is too high to be used in radiation processing applications. This experiment signifies the role of water content to the system.

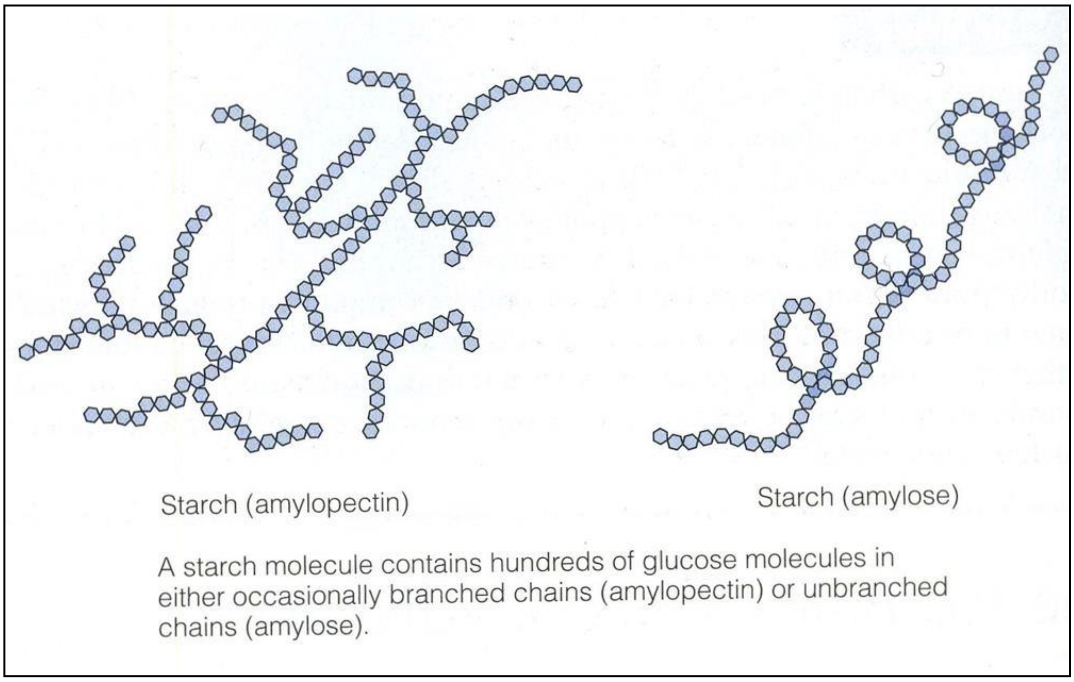
5.3.2 Films based on formation of Starch iodine complex

Water radiolysis leads to formation of hydrogen peroxide along with other oxidising radicals that oxidise iodide to iodine with the help of iodate.

$$H_2O_2(aq) + 3I^-(aq) + 2H^+ \longrightarrow I_3^- + 2H_2O$$

Iodide is converted to triiodide by hydrogen peroxide in the presence of hydronium ions.In radiation chemical pathway, iodide and iodate were found to be reacting with oxidizing species such as perhydroxy radical, hydroxyl radical and hydrogen peroxide to form iodine. Iodine thus formed is converted to soluble triodide ion in presence of iodide present. The triiodide combines with amylose in starch to produce the blue black complex. Since concentration of triiodide produced will be proportional to the amount of dose received, which in turn is proportional to starch iodide complex formed, it can serve as go no-go indicator for radiation processing applications, by indicating the approximate dose received depending on the intensity of colour formed (starch iodide complex). As organic solvents make the test insensitive water based polymer PVA was tried. A film based on water soluble polymer can be cast using the above solution, upon irradiation the film will turn darker with dose thus can serve for assuring quantity of dose received during radiation processing.

Plants store glucose as the polysaccharide starch. Starch can be separated into two fractions-amylose and amylopectin (Figure 5.8). Natural starches are mixtures of amylose (10-20%) and amylopectin (80-90%).Amylose is made up of α (1→4) bound glucose molecules. The carbon atoms on glucose are numbered, starting at the aldehyde (C=O) carbon, so, in amylose, the 1-carbon on one glucose molecule is linked to the 4-carbon on the next glucose molecule (α (1→4) bonds). The structural formula of amylose is represented below in Figure 5.8. The number of repeated glucose subunits (n) is usually in the range of 300 to 3000, but can be many thousands.



A starch molecule contains hundreds of glucose molecules in either occasionally branched chains (amylopectin) or unbranched chains (amylose).

Figure 5.7: Structure of Amylopectin and Amylose starch

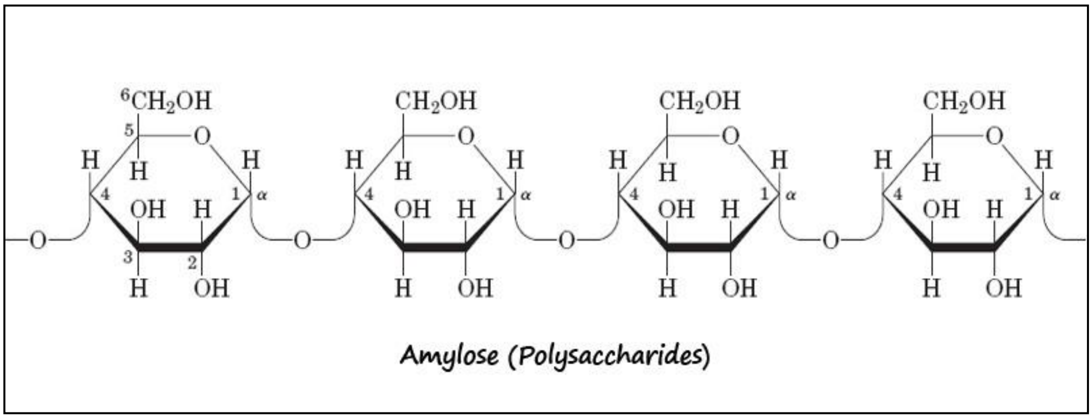


Figure 5.8: Structural formula of amylose

5.3.2.1 **Principle**

5.3.2.1.1 Test for Starch

Amylose in starch is responsible for the formation of a deep blue color in the presence of iodine. The iodine molecule slips inside of the amylose coil. Iodine is not very soluble in water, therefore the iodine reagent is made by dissolving iodine in water in the presence of potassium iodide. This makes a linear triiodide ion complex that is soluble and slips into the coil of the starch causing an intense blue-black color. Starch amylopectin does not give the color, nor does cellulose, nor do disaccharides such as sucrose in sugar. Starch solutions are prepared in distilled water as explained in detail by some authors (Alsberg and Griffing 1926)

5.3.2.1.2 Test for Iodine

Only elemental iodine in the presence of iodide ion will give the characteristic blue black color. Neither iodine alone nor iodide ions alone will give the color result (Rogers 2003). The colour of the starch complex is very deep and can be detected visually at very low concentrations (Svehla 1996). The colour sensitivity decreases with increasing temperature (ten times less sensitive at 50 °C), and upon the addition of organic solvents such as ethanol or propanone.

Starch iodide paper is used for detection for oxidisers, starch iodide paper is made by dipping absorbent paper in solutions of starch and iodide, followed by air drying. The paper on drying is used for testing strong oxidisers such as chlorine gas and nitrites. These oxidisers oxidize iodide to iodine, which in presence of iodide is converted to triodide. Triiodide reacts with amylose of starch to form dark blue-black complex due to trapping of triiodide ions in amylose helix. (IS-2263 1979)

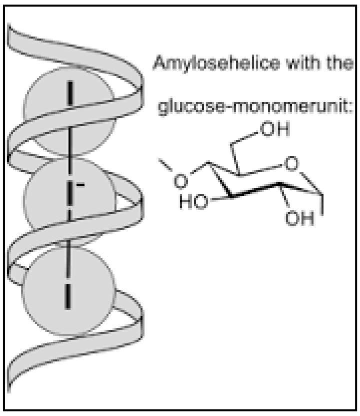


Figure 5.9: Starch iodide blue, Amylose helix with triiodide trapped

5.3.2.2 **Reagents and Preparation**

Iodine iodate in the ratio 2:1, similar to that used in radiochromic solution was used for initial experiments. Soluble starch, (CAS Number 9005-84-9) from sigma Aldrich was used without any further processing. Polyvinyl alcohol solution was prepared as explained for earlier systems. Glycerine was added after dissolution of PVA in water.

Solution containing 2mol/m^3 iodide,1 mol/m^3 iodate and 0.5 % starch in solution were prepared in distilled water.

Films were cast in glass petri dish using 5 % PVA solution having reagent concentrations same as that used in solution form (above).

5.3.2.3 **Irradiation and measurements**

Glycerine was introduced in the solution before films were cast as it was found to serve two purposes in radiochromic systems discussed earlier, first it increases the water content of the films thus increasing formation of water radiolysis products and helping their movement and secondly it increase iodine availability for reaction due to its iodine absorption properties. Additionally it is also used as a plasticizer for polyvinyl alcohol films.

The dried films were peeled off and cut into 2 sq. cm. samples. The films prepared were irradiated using GC-1200 to doses as high as 25 kGy and 50 kGy, however the films did not show any colour change.

It was observed during irradiation of PVA gel there were black spots created intermittently probably due to PVA iodine interactions as PVA combines with iodine by forming complex that can be detected visually (Yoshinaga, et al. 2001).

5.3.2.4 **Results and Discussions**

Experiments performed using solution indicated starch iodide complex formation at 500 Gy dose. The colour of the solution changes from nearly colourless to black after receiving radiation dose. However, Starch was unable to form complex with iodine in PVA film form at the doses studied as no colour change was observed for films irradiated to 50 kGy dose, the most probable reason can be the immobility of triiodide ions due to low water content.

5.3.2.5 **Conclusions**

Although in solution form, there is colour change occurring the complex formed tends to settle in lumps at the bottom of irradiation vessel which may lead to ambiguity in dose assessment. In solid media, this effect might have been taken care however no colour change was observed.

Some higher water retaining polymer film along with halogenation catalyst can be used for the study. Amylose can be tested as replacement of starch to improve sensitivity 5-fold (natural starch has 20 % amylose).

5.4 Development of Bromide based Radiation processing indicator films

The present work relates to development of radiation indicator system for radiation sterilisation (http://www.who.int/en/ n.d.).

Range of color indicator dosimeters of ionizing radiation exist, a majority of them incorporate an acid sensitive dye responsive to ionizing radiation that changes color on exposure to such radiation. Methyl red, methyl orange, dimethyl yellow are few dyes used for the process

The US patent (Panchenkov and Kozlov 1975) discloses a color indicator-dosimeter of ionizing radiation, comprising of two dyes one of which is more sensitive to decolourisation by radiation, resulting in colour change upon irradiation.

This US patent (Feldman, Adair and Hess 1988) discloses a radiation dosimeter comprising a support having a layer of microcapsules on the surface, when exposed to gamma or electron beam radiation, said composition polymerizes and hardens said microcapsules. pH indicator dye based indicators have poor light stability in pre as well as post irradiation condition.

The US patent (Ueno, Katanosaka and Noriko 1992) discusses about a dosimeter which comprises of a polymer containing either halogen atoms and acetic acid groups and a pH-sensitive indicator dye capable of changing color according to the change in pH for easy determination of dose by color change, at high and low doses.

The US patent (Warner and Johns 2003) discloses a dosimeter that detects ionizing radiation, comprising of silver halide salts which reduce proportional to the dose received and become opaque that can be related to the absorbed dose.

Conclusively, in dye based indicator systems, colourisation and decolourisation effect is not specific for high energy radiation leading to discrepancies. A water soluble dye based indicator was tried and results presented.

5.4.1 **Principle**

The experimental work done in this section is based on the principle of halogenation of phenol as given in Figure 5.10. Halogenation of fluorescein leads to formation of loss of fluorescence and formation of coloured derivatives, many commercial methods are known in the field (Singh and Agarwal 2014). The change in colour is proportional to the dose received and can thus act as radiation indicator. A solid polymer media is chosen to contain the reagents. Polymer film is cast using water soluble polymer since water aids movement of ions and reagent species.

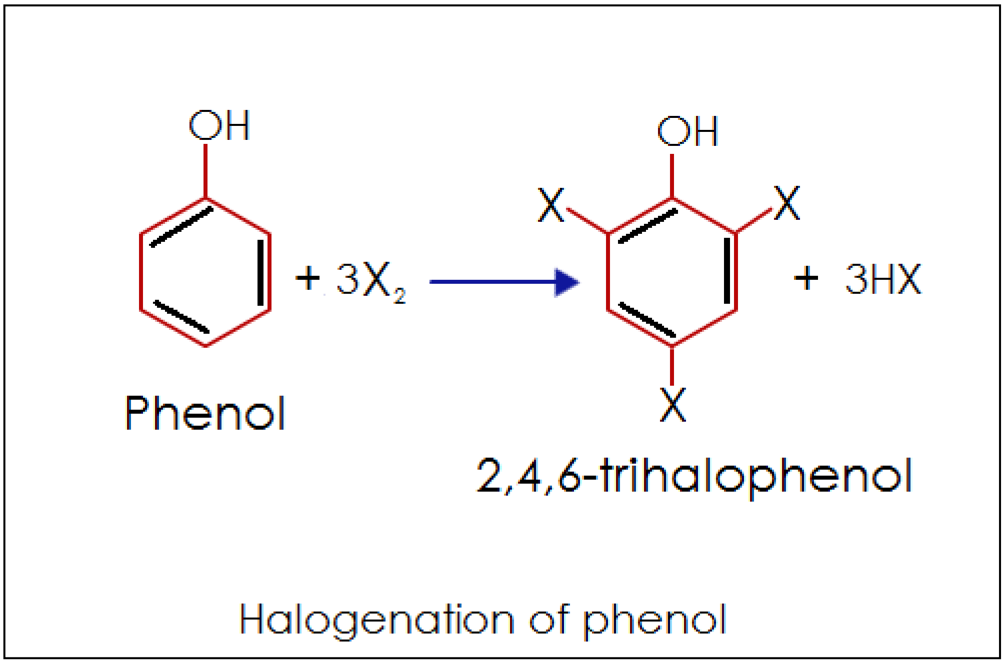


Figure 5.10 Halogenation of phenol (X-halogen)

The –OH group in the phenol is an activating group in the benzene ring which donates electron into the benzene ring to stabilize it. So, the product can be easily to form in the reaction.

The –OH group is ortho - para activating group in the benzene ring. The incoming substituent will go into the ortho position or the para position, but hardly go into the meta position. This is due to the high energy is required for the product with a substituent at meta position to form in the reaction.

The halogen molecules undergo substitution reaction in this reaction by substituting three hydrogen atoms from the benzene ring with three halogen atoms to maintain the aromaticity of the ring in phenol. Process for synthesizing halogenated derivatives of fluorescein for use in the production of non-volatile memory. Patent US 20080061289 A1. 2006.)

Iodination of fluorescein was successfully done in bicarbonate medium by iodide iodate with the help of radiation. Tests for halogens using fluorescein utilise halogens in excited state for halogenations of fluorescein (Vogel 1974). Based on the literature survey, a radiation chemical pathway for fluorescein halogenation was studied (Sworski 1954). The halogenation reaction was carried out in liquid and solid medium to test its feasibility as radiation indicator labels.

5.4.1.1 **Experiment Detail**

Initial experiments were done in aqueous medium with inorganic and organic halogen salts along with uranine. The halogenation occurs in steps similar to that observed during fluorescein iodination. Irradiations were done using gamma chambers in centrifuge tubes in liquid media to test the feasibility of the medium. Parameter studies such as concentration dependence and effect of catalyst were done and composition finalized. The colour of the optimized solution changes from yellow to red on receiving radiation dose (Sjoback, Nygren and Kubista 1995). The above solution was incorporated with polyvinyl alcohol and made into films to test their feasibility in film media. The films were irradiated to increasing doses.

5.4.1.2 **Irradiation and measurements**

All irradiation were carried out using GC-900 and GC -1200. The irradiations were carried out with the films packed in polythene pouches to prevent them from drying and to reduce other environmental effects.

5.4.2 **Results and Discussions**

Upon irradiation films undergo colour change from yellow to light orange (1kGy) that gradually changes to orange (10 kGy) and finally to red (25 kGy) as depicted in Figure 5.11. In solution form the threshold dose required for observing colour change was much lower as compared to films.

The films can be used as go no-go radiation processing indicators. The colour developed due to formation of halogen derivative of fluorescein is irreversible and stable upto six months. The indicators are easy to prepare and made using simple chemicals. Scaled up version can be used for commercial manufacture as readily usable radiation processing indicators. Storage should preferably done in dark conditioned environment with low temperature gradients.

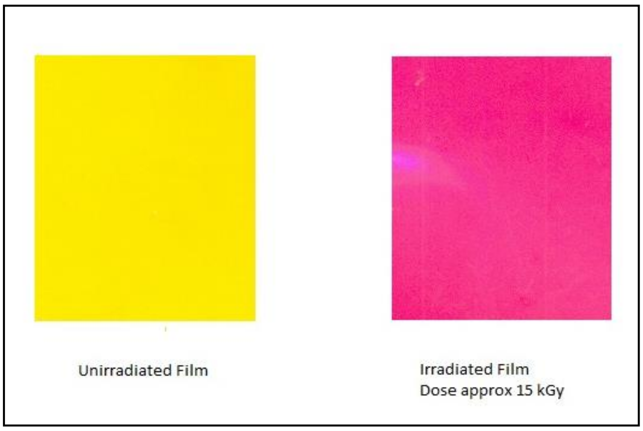


Figure 5.11: Actual photograph of radiation processing indicator film

5.4.3 **Conclusions**

Radiation indicator film was prepared using water soluble polymer PVA and relatively nontoxic chemicals. The said indicators can be affixed externally to identify and segregate radiation processed products.

a) A film based radiation indicator system to ascertain minimum dose received during radiation processing is developed using simple techniques and inexpensive chemicals.

b) The indicator can be used for radiation sterilization applications (25 kGy)

c) Colour change is permanent and irreversible.

d) Unirradiated film indicators should be stored in dark conditions with low temperature gradient surroundings.

e) Indicators are stable for more than six months

f) Indicators developed indigenously can be used as go no-go indicators for gamma radiation processing facilities.

Chapter 6 Conclusions, future perspectives and summary

6.1 Ferrous Sorbitol Xylenol Orange dosimeter for low dose estimation

Chapter 3 discribes development of a new low dose dosimeter (0.1 Gy to 12 Gy) based on enhancement of ferrous ion oxidation by sorbitol and complexation of ferric formed with xylenol orange. Ferric xylenol orange being a stable complex with high molar absorption coefficient low doses can be measured accurately. The dose absorbance relation is linear upto 8 Gy of absorbed dose.

The study suggest, sorbitol can be used as a radiolytic sensitizer in FSX dosimeter that can be used for low level radiation dosimetry applications with high reproducibility. The dosimeter can be used for calibration of low dose irradiators such as blood irradiators and gamma chambers. It is recommended to the user to establish dose absorbance relation before estimation of doses.

6.2 Radiation indicator liquid

Chapter 4 (section 4.3) describes development of a new radiation chemical technique for erythrosine synthesis. The iodide-iodate reaction was used for fluorescein iodination with bicarbonate as driving ion. It was found that borax and molybdenum enhanced the reaction. The fluorescent yellow solution becomes orange and gradually through shades of orange becomes red. The change in colour is related to iodination of fluorescein in stages of mono, di, tri- iodo fluorescein with erythrosine as the final product. The optimum parameters were finalized and method can be scaled up for commercial purposes. Relatively pure samples of erythrosine can be prepared using the method without the use of catalyst or iodine. As the colour developed on iodination of fluorescein is step wise process, the system was tested to be used as radiochromic system.

Concentration of components was finalized and radiation processing indicator liquid developed is ready to be used without any further modifications. However for adjusting the response of the dosimeter for a particular threshold, concentration of the reagents can be adjusted as explained.

6.3 Radiochromic Dosimeter

Chapter 4 (section 4.4) describes development of a radiochromic dosimeter (200 Gy- 2500 Gy). The system shows good pre and post irradiation stability and reproducible results. The radiochromic dosimeter developed has no special requirement of glass container or triple distilled water for solution preparation as required by currently used systems. Solutions are made using single distilled water and irradiation can be performed in polymer containers (polypropylene). The cost effective dosimeter solution will be less than 5 rupees (per 5 ml) for single dose measurement. All absorbance measurements can be done using standard spectrophotometer using standard glass or perpex cuvettes. Refrigeration of solutions is highly recommended and net absorbance of the solutions should be used for dose estimation. The user is advised to prepare fresh dose absorbance relation before estimating and reporting doses.

Toxic cyanide used in commercial radiochromic systems like FWT-60 is elimnated. Standard colourimeter or spectrophotometer can be used for evaluation of dose as compared to requirements of special instruments by available imported systems. Optichromic solutions are contained in specially manufacture waveguides for proper storage and handling, no special packaging is required and unirradiated solutions can be stored in glass vessels or polypropylene tubes that are available easily.

Thus the indigenously developed system provides a low cost alternative to the imported patented systems currently used for dosimetry in India.

6.4 Radiation indicator gel

Chapter 5 describes development of a new radiation indicator gel (200 Gy - 10 kGy). In this system, polyvinyl alcohol was added to radiochromic solution with borax as catalyst. As borax cross links PVA in presence of alkali, there is formation of gel. The concentration of PVA and radiochromic solution for formation of gel was finalized.

Radiochromic gel was developed to provide visual identification of radiation processed products. The gels are made from relatively non-toxic and easily available chemicals.

The dose range is from 200 Gy to 10 kGy, there is gradual development of colour with dose, the colour of the gel changes from fluorescent yellow to orange that gradually turns red on receiving around 10 kGy dose.

Dose rate effect was not observed in the range 10-40 Gy/min. Post irradiation colour change is stable for more than 12 months. The instantaneously development of colour upon receiving dose is irreversible. The gels can be kept inside the carton before irradiation in sealed plastic pouches. The gel based system is non spillable and can be filled in polythene bags or polymer tubes. As the gels are relatively nontoxic they can be disposed off as polymer waste.

Radiation indicator gel is stable for more than 12 months. The gel should preferably be stored in dark conditions between 5 to 25^{o}C to prevent localisation of dye and chemicals and to avoid dehydration of the gel. Environments with high temperature gradients should be avoided for storage. Radiochromic gels can be used for assessment of dose and stored for keeping record.

6.5 Radiation processing indicator film (Label)

Water soluble polymer based radiation indicator film was developed to be used as radiation indicator label in radiation processing facilities(200 Gy to 15 kGy) .The films are based on halogenations of xanthenes dyes based on studies conducted earlier.

The films can be used as go no-go radiation processing indicators. The colour developed is stable (upto six months) and irreversible. The indicators are easy to prepare and made using simple chemicals. Scaled up version can be used for commercial manufacture as readily usable radiation processing indicators. Storage should preferably be done in dark conditioned environment with low temperature gradients. The developed indicators can be used for radiation processing of medical products (25 kGy - sterilization dose) to indicate sterilization.

6.6 Some ideas worked in a different way

System based on the principle of Schiff's aldehyde detection was found to be quite unstable both in liquid and film form. In liquid form the post irradiation products tend to adhere walls of the container while in the film form the stability is very low.

Different aqueous and non-aqueous base polymers can be tried for this system. Also dyes other than pararosaniline that are used to make Schiff-type reagents, for e.g. Acriflavine, , Azure A and C, Crystal violet, Methyl violet, Methylene blue, Safranin O, Thionin and Toluidine blue can be used.

For radiation indicators based on starch iodide test, since positive results were not obtained in the film medium the work was discontinued to try out new systems, however further studies can be done using higher water retaining film forming polymers with special preference given to biodegradable polymers.

6.7 Future perspectives

Tests for studying the effect of influencing factors on the systems are to be done to establish their response. The radiation indicator developed in liquid and gel form is to be tested for field performance.

Similarly, experiments are to be performed to establish radiochromic dosimeters. The system after establishing can be applied to radiation processing industry for carrying out routine dosimetry.

The film based radiation indicator system can be designed to make self-sticking labels. With colour chart providing change in colour occurring with radiation dose they can be used to roughly estimate the amount of dose received. The composition can be explored further for modification to alter the detection threshold and dose range.

6.8 Summary

i. FSX dosimeter developed can be used for low dose dosimetry with high reproducibility in the range 0.2 Gy to 12 Gy.

ii. The radiation indicator solution can be used for experiments and demonstrations to research students as an inexpensive alternative to radiation indicator label.

iii. Radiation indicator gel is more stable as compared to solution before and after irradiation. Radiation indicators presently used are imported systems that are patented. The developed liquid and gel provides an indigenous solution.

iv. The radiochromic dosimeter provides a simple and relatively non-toxic alternative to expensive patented commercially available imported systems. The dose range covered is 250 Gy to 2500 Gy, filling up the gap of unavailability of indigenous dosimeters in this range. This dose range covers radiation processing applications like mango irradiation for quarantine treatment, rice and pulses irradiation for insect disinfestation and other low dose applications.

v. Radiation indicator film developed can be used as go no-go label for indicating proper dose delivery to products.

vi. Several new gamma and electron beam radiation processing facilities are coming up in Bharat (India), the systems developed in the present study will provide them with indigenous dose assessment systems.

vii. In summary, goal of the thesis to develop radiation dosimeters and radiation indicators for radiation processing applications has been fulfilled.

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