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IDENTIFICATION OF IRRADIATED FOOD BY THERMOLUMINESCENCE METHOD

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Identification of Irradiated Food by Thermoluminescence Method

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Supervisor
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by
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ABSTRACT

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M.Sc. in Engineering Physics
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The purpose of this study is to give general and technical information about food irradiation and the detection of irradiated food by thermoluminescence technique (TL). Two types of dried legumes were used to identify the irradiated and unirradiated foods by TL technique. These spices are corn and chickpea which were packed in polyethylene bags and irradiated using a ^{60}Co source with dose of 1, 4, 8, 10 kGy, respectively, with a dose rate of ≅1kGy/h. The TL method requires that the inorganic components be separated from the samples. Separation of the organic and inorganic phases was made by using a chemical method. Then, the samples were dried and stored at room temperature in dark region. TL measurement was carried out using a TL reader at a heating rate 1 ^{0}C/sec between room temperature and 400^{0}C. The light emission was recorded in a temperature-dependent mode as a glow curve and was measured in units of nano coulombs (nC).

It was observed that the extracted samples from both legumes exhibit good TL Intensity and the TL intensity of glow curves of them increased proportionally to irradiation doses. Maximum TL temperatures of all irradiated samples are found to be between the 250-280 ^{o}C temperature intervals, it was also found that unirradiated samples did not exhibit any glow peaks.

Key Words: Food irradiation, thermoluminescence, TL measurement, glow curve.

ÖZET

TERMOLÜMİNESANS METODU İLE IŞINLANMIŞ GIDALARIN BELİRLENMESİ

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Bu çalışmanın amacı gıdaların ışınlanması hakkında genel ve teknik bilgi vermek ve ışınlanmış kuru gıda numunelerinin termolüminenans dedeksiyon methodu ile incelemektir. Bu numuneler (iki çeşit kuru gıda; kurutulmuş bakliyat (mısır ve nohut)) naylon poşetlerle paketlenip, ^{60}Co kaynağı ile sırasıyla 1, 4, 8, 10 kGy radyasyon dozuna 1kGy/saat oranında maruz bırakılmıştır. TL metodu örneklerin inorganik kısımlarına uygulanacağından dolayı örneklerin inorganik kısımlarına ihtiyaç bulunmaktadır. Bu nedenle kimyasal metot kullanılarak örnekler organik ve inorganik kısımlarına ayrıştırılmıştır. Daha sonra örnekler karanlıkta ve oda sıcaklığında kurutularak depolanmıştır. TL ölçümleri TL okuyucusu ile ısıtma oranı 1^{0}C/sec. kullanılarak oda sıcaklığı ile 400^{0}C arasında yapılmıştır. Yayılan ışımanın sıcaklığa bağlı olarak ışıldama eğrileri nano kulon (nC) birimi olarak ölçülmüş ve kayıt edilmiştir.

Her iki kuru bakliyattan elde edilen örneklerin TL ışıldama şiddetlerinin iyi olduğu ve artan radyasyonlama dozu ile birlikte ışıldama şiddetinin arttığı gözlenmiştir. Işınlanan tüm örneklerin maksimum TL sıcaklıklarının 250-280 ^{o}C arasında olduğu bulunmuştur. Ayrıca ışınlanmayan örneklerin herhangi bir ışıldama eğrisi vermediği gözlenmiştir.

Anahtar Kelimeler: Gıda ışınlanması, termoluminesans, TL ölçümü, ışıldama eğrisi.

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CHAPTER 1

1.1 Introduction

Thermoluminescence (TL) is the physical phenomenon in which a solid sample absorbs energy while irradiated at a given temperature, and releases this energy in the form of light while heating the sample. The emitted light is recorded as intensity vs. temperature in the shape of one or more TL peaks. Under favorable conditions, the emitted TL light intensity is proportional to the absorbed dose, and thus, using an appropriate calibration, one can evaluate the applied dose in the given radiation field. The TL signal may be the intensity at the maximum or the area under the TL glow peak, which are usually nearly proportional to each other. In “regular” dosimetric applications, one can choose an appropriate material with reproducible results in repeated measurements, linear dose dependence for the kind of radiation in question as well as dose-rate independence and long time stability. The situation is significantly more complicated in retrospective dosimetry such as in accident dosimetry where the exposure to radiation is to be determined by using existing materials such as porcelain [1].

All buried materials are exposed to a constant flux of ionising radiation. This radiation originates from naturally occurring radioactivity, which is present in all deposits, and from cosmic radiation. When crystalline materials are exposed to ionising radiation, a redistribution of electrical charge takes place within the crystal. Much of the displaced charge finds its way back to its original state within a short space of time, but a small fraction of it can become trapped for long periods in higher energy states. In this way the crystal can be said to retain a memory of the ionising radiation to which it has been exposed.

The extra energy that the crystal contains as a result of the radiation exposure can be released by heating the material. When heat is applied, some of the released energy appears in the form of light, causing the material to luminesce. If the crystal is then cooled and re-heated it does not re-emit light, because the energy excess which produced the first emission has now been released from the crystal. This effect is known as thermoluminescence. It appears only while irradiated crystals undergo a progressive temperature increase, and should not be confused with incandescence, which is the light radiated continuously by hot bodies.

The graph which traces the variation of the TL intensity with increasing temperature is known as the *glow curve* of the sample. In general, the glow curve exhibits one or more peaks, which occur whenever the increasing thermal energy of the crystal becomes sufficient to release electrical charge from the various traps in which it is held.

The glow curves illustrate how the intensity of the TL peak grows as the radiation exposure increases. The TL emission produced by the unirradiated portions is known as the *natural TL*, since it results from the radiation dose accumulated by the sample in the natural environment over geological time.

Thermoluminescence analysis is used to detect radiation processing of foods which are contaminated with sand or dust. Silicate minerals are isolated, their radiation-induced luminescence is measured and compared to the thermoluminescence from a second measurement after exposure to a defined radiation dose (normalization).

The occurrence of intense TL in artificially irradiated natural minerals enables an easy readout of even minute amounts of mineral particles. Both siliceous and carbonate minerals are TL-sensitive. Calcium carbonate biominerals may show this sensitivity as well. The TL signals are relatively stable against storage and ambient light. Therefore, TL identification by readout of mineral particles has already been established as approved method for spices and marine animals.

Irradiation is a process of exposing substances to radiant energy. A more specific and practical description for food irradiation is a process of exposing food to radiant (ionizing) energy for a specified length of time. The amount of exposure is controlled to produce various preservation effects including killing microorganisms that cause spoilage or disease as well as killing insects in foods such as grains or spices.

The radiant energy used in the process is very short light waves with very high energy (gamma rays, X-rays or electron beams). The energy is emitted from machines that produce electron beams or X-rays or from radioactive materials like cobalt-60 or cesium-137 that emit gamma rays. The waves can pass through packaging and some of the energy is absorbed by molecules in the food or living organisms.

Food irradiation currently has a 50-year history of scientific research and testing, with more than 40 years preceding approval of the process for any foods in the United States. To date, no other food technology has had as long a history of scientific research and testing before gaining approval.

In food irradiation, the radiation "dose" that a food receives should not be confused with something added to the food. The "dose" for food irradiation is the amount of radiation absorbed by the food and it is not the same as the level of energy transmitted from the radiation sources. The dose is controlled by the intensity of radiation and the length of time the food is exposed.

Terms used to describe this "dose" or amount of absorbed radiation, are unfamiliar and confusing to most people. In the past, the term used was rad, short for "radiation absorbed dose," which is 100 ergs absorbed by 1 gram of matter. The rad has been replaced by the gray (Gy). One gray is equal to 100 rads or 0.00024 Calorie (i.e., diet calorie) per kilogram of food (0.00024 Calorie per kilogram equals 0.0001 Calorie per pound). The FDA's regulations describe radiation levels in terms of the kilogray (kGy), equal to 1000 Gy.

When radiation energy is absorbed by food, it causes a variety of chemical and physical reactions. The amount of energy the food absorbs is controlled so the changes produced have desirable food preservation effects while maintaining the safety, quality, and wholesomeness of the food. The food itself does not become radioactive.

In this study focuses on (i) the confirmation of the validity of TL as a method to discriminate between irradiated and non-irradiated irradiated chickpea and corn; (ii) the characterization of the TL glow peaks;(iii) the determination of the dependence of TL intensity with different doses; and (iv) the modeling, from irradiated samples, of the stability of TL signal with time. This study wil carried out to establish a detection method for irradiated legumes (chickpea and corn) through thermoluminescence (TL). The legumes will packed in polyethylene bags and will irradiated using a ^{60}Co source with dose of 1, 4, 8 and 10 kGy, respectively. The TL kinetic (trapping) parameters of overlapping peaks will estimated by computerized glow curve deconvolution (CGCD) method.

1.2 LITERATURE SURVEY

1.2.1 The Food Irradiation Process

Three different irradiation technologies exist, that use three different kinds of rays: gamma rays, electron beams and x-rays. The first technology uses the radiation given off by a radioactive substance. This can be either a radioactive form of the element cobalt (Cobalt 60) or of the element cesium (Cesium 137). These substances give off high energy photons, called gamma rays, which can penetrate foods to a depth of several feet. These particular substances do not give off neutrons, which means they do not make anything around them radioactive. This technology has been used routinely for more than thirty years to sterilize medical, dental and household products, and it is also used for radiation treatment of cancer. Radioactive substances emit gamma rays all the time [1]. When not in use, the radioactive "source" is stored down in a pool of water which absorbs the radiation harmlessly and completely. To irradiate food or some other product, the source is pulled up out of the water into a chamber with massive concrete walls that keep any rays from escaping. Medical products or foods to be irradiated are brought into the chamber, and are exposed to the rays for a defined period of time. After it is used, the source is returned to the water tank.

Electron beams, or e-beams, are produced in a different way. The e-beam is a stream of high energy electrons, propelled out of an electron gun. This electron gun apparatus is a larger version of the device in the back of a TV tube that propels electrons into the TV screen at the front of the tube, making it light up. This electron beam generator can be simply switched on or off. No radioactivity is involved. Some shielding is necessary to protect workers from the electron beam, but not the massive concrete walls required to stop gamma rays. The electrons can penetrate food only to a depth of three centimeters, or a little over an inch, so the food to be treated must be no thicker than that to be treated all the way through [2]. Two opposing beams can treat food that is twice as thick. E-beam medical sterilizers have been in use for at least fifteen years.

The newest technology is X-ray irradiation. This is an outgrowth of e-beam technology, and is still being developed. The X-ray machine is a more powerful version of the machines used in many hospitals and dental offices to take X-ray pictures. To produce the X-rays, a beam of electrons is directed at a thin plate of gold or other metal, producing a stream of X-rays coming out the other side. Like cobalt gamma rays, X-rays can pass through thick foods, and require heavy shielding for safety. However, like e-beams, the machine can be switched on and off, and no radioactive substances are involved. Four commercial X-ray irradiation units have been built in the world since 1996.

Two things are needed for the irradiation process; one of them is a source of radiant energy, and another is a way to confine that energy. For food irradiation, the sources are radioisotopes (radioactive materials) and machines that produce high-energy beams. Specially constructed containers or compartments are used to confine the beams so personnel won't be exposed. Radioisotopes are used in medical research and therapy in many hospitals and universities. They require careful handling, tracking, and disposal. Machines that produce high-energy beams offer greater flexibility [3]. For example, they can be turned on and off unlike the constant emission of gamma rays from radioisotopes.

Irradiation is known as a cold process. It does not significantly increase the temperature or change the physical or sensory characteristics of most foods. An irradiated apple, for example, will still be crisp and juicy. Fresh or frozen meat can be irradiated without cooking it. During irradiation, the energy waves affect unwanted organisms but are not retained in the food. Similarly, food cooked in a microwave oven, or teeth and bones that have been x-rayed do not retain those energy waves [4] .

Thermoluminescence analysis is used to detect radiation processing of foods which are contaminated with sand or dust. Silicate minerals are isolated, their radiation-induced luminescence is measured and compared to the thermoluminescence from a second measurement after exposure to a dexned radiation dose (normalization). In the present study, the mineral mixture and its main components feldspar and quartz were investigated for their thermoluminescence behaviour using different types of radiation, in order to determine adequate radiation sources for the purpose of normalization. The material was irradiated with types of ionizing radiation commonly used for commercial food irradiation, i.e. accelerated electrons with beam energies of 5 MeV as well as 10 MeV, and ^{60}Co gamma-rays.

After thermoluminescence measurements, samples were re-irradiated using either accelerated electrons with beam energies of 2 MeV, 5 MeV or 10 MeV, or ^{60}Co-γ-rays, ^{90}Sr-β-rays or ultraviolet rays (200-280 nm). Evaluation of the first and corresponding second glow curve revealed that their shapes depend on the type of minerals in the mixture. The second radiation treatment (normalization) is satisfactory when accelerated electrons (2, 5 and 10 MeV) as well as^{60}Co-γ-rays and ^{90}Sr-β-rays are employed. Normalization with ultraviolet rays, however, has only a limited range of use [5].

Irradiation exposes food to radiant energy. Food is passed through an irradiator--an enclosed chamber--where it is exposed to a source of ionizing energy. The sources of ionizing energy may be gamma rays from cobalt 60 (^{60}Co), cesium 137 (^{137}Cs), x-rays, or electrons generated from machine sources [3,4]. The emitted gamma rays are very short wavelengths, similar to ultraviolet light and microwaves. Because gamma radiation does not elicit neutrons (ie, the subatomic particles that can make substances radioactive), irradiated foods and their packaging are not made radioactive [4,5].

A self-contained, prefabricated cabinet loaded with ^{137}Cs to provide an additional processing option is being developed. Electron beam facilities, widely used to irradiate medical equipment, have been built for food treatment. Energy penetration is about $1^1/_2$ inches in food products, so the thickness of items to be treated is limited to about 3 inches with double-sided treatment. A combination electron beam and x-ray facility for food irradiation is being planned for construction in the northeastern United States. Regardless of source, the effect of ionizing energy on food is identical. Energy penetrates the food and its packaging but most of the energy simply passes through the food, similar to the way microwaves pass through food, leaving no residue. The small amount of energy that does not pass through the food is negligible and is retained as heat [6,7].

The duration of exposure to ionizing radiation, density of food, and the amount of energy emitted by the irradiator determine the amount or dose of radiant energy to which the food is exposed [4,5,6]. Food irradiation does not replace proper food production or handling. Even with treatments that destroy 99.9% of a pathogen, some could still survive [4]. Bacteria that cause spoilage are more resistant to irradiation than pathogens and require a higher treatment. Therefore, the handling of foods processed by irradiation should be governed by the same food safety precautions as all other foods. Food irradiation cannot enhance the quality of a food that is not fresh or prevent contamination that occurs after irradiation.

Radiation is broadly defined as energy moving through space in invisible waves. Radiant energy has differing wavelengths and degrees of power. Light, infrared heat, and microwaves are forms of radiant energy. So are the waves that bring radio and television broadcasts into our homes. Broiling and toasting use low-level radiant energy to cook food. The radiation of interest in food preservation is ionizing radiation, also known as irradiation [8]. These shorter wavelengths are capable of damaging microorganisms such as those that contaminate food or cause food spoilage and deterioration. That capability, plus the fact that much of our food supply is lost due to spoilage and insects each year is why scientists have been experimenting with irradiation as a method of food preservation since 1950. They have found irradiation to be a controlled and very predictable process.

Irradiation can be used to destroy or inactivate organisms that cause spoilage and decomposition, thereby extending the shelf life of foods. It is an energy-efficient food preservation method that has several advantages over traditional canning. The resulting products are closer to the fresh state in texture, flavor, and color. Using irradiation to preserve foods requires no additional liquid, nor does it cause the loss of natural juices. Both large and small containers can be used and food can be irradiated after being packaged or frozen.

Foods that are sterilized by irradiation can be stored for years without refrigeration just like canned (heat sterilized) foods. With irradiation it will be possible to develop new shelf-stable products. Sterilized food is useful in hospitals for patients with severely impaired immune systems, such as some patients with cancer or AIDS. These foods can be used by the military and for space flights. In this role, irradiation offers an alternative to chemicals for use with potatoes, tropical and citrus fruits, grains, spices, and seasonings. However, since no residue is left in the food, irradiation does not protect against reinfestation like insect sprays and fumigants do.

Irradiation can be used to effectively eliminate those pathogens that cause foodborne illness, such as Salmonella [7-9]. All methods used to process and preserve foods have benefits and limitations.Opponents of irradiation worry that these radiolytic products are hazardous. Biochemical and biomedical tests have not been able to identify any health problems or ill effects associated with tested radiolytic compounds.

Irradiated food does not become radioactive. At the radiation energy levels used in food processing, only chemical changes are possible, not nuclear changes that would make the food itself radioactive. Over 35 years of research suggest that the chemical by-products of radiation ("radiolytic products") are mostly the same as by-products of conventional cooking or other preservation methods. Animal feeding studies show no toxic, teratogenic or mutagenic effects from irradiated foods. In addition, irradiation leaves no chemical residues in food.

Food irradiation is a promising new food safety technology that can eliminate disease-causing germs from foods. Like pasteurization of milk, and pressure cooking of canned foods, treating food with ionizing radiation can kill bacteria and parasites that would otherwise cause foodborne disease. The food that NASA astronauts eat has been sterilized by irradiation to avoid getting foodborne illness in space [7]. The effects of irradiation on the food and on animals and people eating irradiated food have been studied extensively. These studies show clearly that when irradiation is used as approved on foods:

- disease-causing germs are reduced or eliminated
- the food does not become radioactive
- dangerous substances do not appear in the foods
- the nutritional value of the food is essentially unchanged

Irradiation is a safe and effective technology that can prevent many foodborne diseases [8].

1.2.2 Historical Summary of Food Irradiation

Early in the 1920s, a French scientist discovered that irradiation could be used to preserve food. This technology was not adopted in the U.S. until World War II. At this time there was a need to feed millions of men and women in uniform. The U.S. Army sponsored a series of experiments with fruits, vegetables, dairy products, fish and meats. In 1963, the U.S. saw its first approval of food irradiation when Food and Drug Administration (FDA) approved its use to control insects in wheat and wheat flour. In 1964, additional approval was given to inhibit the development of sprouts in white potatoes [9-11].

In 1983, approval was granted to kill insects and control microorganisms in a specific list of herbs, spices and vegetable seasonings. (The approved list of food products has been increased with later changes.) Then, in 1985, treatment of pork to control trichinosis was added to the list of approvals. In the same year, approval was granted to control insects and microorganisms in dry enzyme preparations used in fermentation-type processes [9]. In 1986, approval was granted to control insects and inhibit growth and ripening in such foods as fruits, vegetables and grains.

Approval was granted in May, 1990, for irradiation of packaged fresh or frozen uncooked poultry. FDA supports it as an effective control of microorganisms responsible for a major portion of foodborne illness, including *Salmonella, Yersinia,* and *Campylobacter* [11].

Over the last fifty years, thermoluminescence (TL) has developed into a powerful methodology with many different application fields such as: a) radiation dosimetry, including clinical applications, e.g. therapeutical treatment of cancer patients; b) age determination in archaeology and geology; c) mineral prospecting, e.g. for uranium sources; d) study of meteorites and lunar material; e) solid-state defect structure analysis and f) other applications [10,11,12]. An early application of thermoluminescence related to food was described by Chadwick and Oosterheert in 1967, who measured the thermoluminescence of tomato seeds irradiated at liquid nitrogen temperature with x-rays at 0.05-1.0 kGy [13].

To use thermoluminescence as a detection means for irradiated food was first proposed by Heide and BoK gl in 1984 [14]. They suggested detecting the radiation treatment of spices and herbs by investigating whole samples: a few mg of spices were heated in a commercial TL reader usually employed for dosimetry and the light emission recorded as a function of increasing temperature of the spice sample [14]. This led to the idea that spices and herbs themselves may exhibit thermoluminescence. In some interlaboratory studies [15,16], large inter-sample variations were observed. In 1989, Sanderson *et al.* reported that the origins of luminescence are contaminating minerals (sand and dust) in the spice samples. There upon, the mineral grains were isolated for TL analysis. The detection of radiation treatment was improved by normalization, i.e. re-irradiation of the minerals [17, 18]. This second irradiation of the isolated mineral grains fixed on a stainless steel disc for TL measurement allows for differences in mineral composition, e.g. feldspar and quartz and the different mineral weights. In 1895, Wiedemann and Schmidt observed artificially induced luminescence produced by cathode rays in a large number of substances, e.g. alkali halides, by heating; they called it thermoluminescence [9].

The first and second glow curves are compared and the ratio of integrated TL intensities of Glow 1 to Glow 2, evaluated over a defined temperature interval is calculated. This TL glow ratio, thus obtained, is used to indicate radiation treatment of the food, since the population of irradiated samples in principle yields higher TL glow ratios than that of nonirradiated samples. Glow shape parameters offer additional evidence for identifying irradiated foods. After these modifications, the method was extended to other food items carrying concomitant minerals, e.g. potatoes [19], strawberries and mushrooms [20,21], onions, mangoes and papayas [21] as well as shellfish [19,22]. Successful interlaboratory tests with herbs and spices as well as their mixtures [23,24] and shrimps [25,26] led to the adoption of the method for these food items as a European Standard in 1996 [27], and nowadays it is used routinely in food control laboratories. However, to some of these laboratories the normalization step presents problems, because they do not have suitable facilities for the second, normalizing irradiation. They have to send their discs with isolated silicate minerals to other facilities in the region. This shipment may lead to loss of minerals from the discs and may cost much time

Research has been comprehensive and has included toxicological and microbiological evaluation, as well as testing for wholesomeness. In 1955, the US Army Medical Department began to assess the safety of types of foods commonly irradiated in the US diet [28]. Petitions to the Food and Drug Administration (FDA) for approval of specific foods for irradiation soon followed; wheat and wheat powder received first approval in 1963. In the early 1970s, the National Aeronautics and Space Administration adopted the process to sterilize meats for astronauts to consume in space, and this practice has continued [29].

The first products approved by the FDA were wheat and white potatoes in the 1960s. During the 1980s, the FDA approved petitions for irradiation of spices and seasonings, pork, fresh fruits, and dry or dehydrated substances. Poultry received FDA approval in 1990; red meats were approved in 1997. Worldwide, 40 countries permit irradiation of food, and more than half a million tons of food are irradiated annually [30,31,32]. The United States has approximately 40 licensed irradiation facilities; most are used to sterilize medical and pharmaceutical supplies. Food irradiation has an impressive list of national and international endorsements: ADA, Centers for Disease Control and Prevention, American Council on Science and Health, American Medical Association (AMA), American Veterinary Medical Association, Council for Agricultural Science and Technology, International Atomic Energy Agency, Institute of Food Technologists, Scientific Committee of the European Union, United Nations Food and Agricultural Organization (FAO), and World Health Organization (WHO) [33,34].

The nutritional value of the foods are not changed in and they are not made dangerous as a result of the irradiation. The high energy ray is absorbed as it passes through food, and gives up its energy. The food is slightly warmed. Some treated foods may taste slightly different, just as pasteurized milk tastes slightly different from unpasteurized milk. If the food still has living cells, (such as seeds, or shellfish, or potatoes) they will be damaged or killed just as microbes are. This can be a useful effect. For example, it can be used to prolong the shelf life of potatoes by keeping them from sprouting. The energy can induce a few other changes. At levels approved for use on foods, levels of the vitamin thiamine are slightly reduced. This reduction is not enough to result in vitamin deficiency. There are no other significant changes in the amino acid, fatty acid, or vitamin content of food. In fact, the changes induced by irradiation are so minimal that it is not easy to determine whether or not a food has been irradiated.

Irradiated foods need to be stored, handled and cooked in the same way as unirradiated foods. They could still become contaminated with germs during processing after irradiation, if the rules of basic food safety are not followed. Because the irradiated foods have fewer microbes of all sorts, including those that cause spoilage, they may have a longer shelf life before spoiling.

The safety of irradiated foods has been studied by feeding them to animals and to people. These extensive studies include animal feeding studies lasting for several generations in several different species, including mice, rats, and dogs. There is no evidence of adverse health effects in these well-controlled trials. In addition, NASA astronauts eat foods that have been irradiated to the point of sterilization (substantially higher levels of treatment than that approved for general use) when they fly in space. The safety of irradiated foods has been endorsed by the World Health Organization (WHO), the Centers for Disease Control and Prevention (CDC) and by the Assistant Secretary of Health, as well as by the U.S. Department of Agriculture (USDA) and the Food and Drug Administration (FDA).

CHAPTER 2

THEORY OF THERMOLUMINESCENCE

2.1. Basic concepts of thermoluminescence

The phenomenon thermoluminescence has been known for a long time. The first application of this phenomenon for dosimetric purposes was from Daniel et al. [35]. Since then much research has been carried out for a better understanding and improvement of the material characteristics as well as to develop new TL materials. Nowadays, thermoluminescence dosimetry (TLD) is a well-established dosimetric technique with applications in areas such as personnel, environmental and clinical dosimetry.

Thermoluminescence is the physical phenomenon in which a solid sample absorbs energy while irradiated at a given temperature, and releases this energy in the form of light while heating the sample. The emitted light is recorded as intensity vs. temperature in the shape of one or more TL peaks. Under favorable conditions, the emitted TL light intensity is proportional to the absorbed dose, and thus, using an appropriate calibration, one can evaluate the applied dose in the given radiation field. The TL signal may be the intensity at the maximum or the area under the TL glow peak, which are usually nearly proportional to each other. In "regular" dosimetric applications, one can choose an appropriate material with reproducible results in repeated measurements, linear dose dependence for the kind of radiation in question as well as dose-rate independence and long time stability.

Food is irradiated to provide the same benefits as when it is processed by heat, refrigeration, freezing or treated with chemicals to destroy insects, fungi or bacterial that cause food to spoil or cause human disease and to make it possible to keep food longer and in better condition in warehouses and homes. Because irradiation destroys disease-causing bacteria and reduces the incidence of food borne illness, hospitals sometimes use irradiation to sterilize food for immuno-compromised patients.

Irradiated foods are wholesome and nutritious. All known methods of food processing and even storing food at room temperature for a few hours after harvesting can lower the content of some nutrients, such as vitamins. At low doses of radiation, nutrient losses are either not measurable or, if they can be measured, are not significant. At the higher doses used to extend shelf-life or control harmful bacteria, nutritional losses are less than or about the same as cooking and freezing.

Radioactivity in foods can occur by two routes: contamination of foods with radioactive substances or by penetration of energy into the nuclei of the atoms that make up the food. The irradiation process involves passing food through an irradiation field; however, the food itself never contacts a radioactive substance. Also, the ionizing radiation used by irradiators is not strong enough to disintegrate the nucleus of even one atom of a food molecule.

Federal government and other scientists reviewed several hundred studies on the effects of food irradiation before reaching conclusions about the general safety of the treatment. In order to make recommendations specifically about poultry irradiation, U.S. Food and Drug Administration scientists reviewed findings form additional relevant studies. Independent scientific committees in Denmark, Sweden, United Kingdom and Canada also have reaffirmed the safety of food irradiation. In addition, food irradiation has received official international endorsement from the World Health Organizations and the International Atomic Energy Agency. Irradiation, at the levels normally used in food processing, destroys most, but not necessarily every single microorganism present; it does not sterilize the food.

As with any food, consumers must take appropriate precautions, such as refrigeration and proper handling and cooking, to make sure that potentially harmful organisms do not present a problem. After treatment, the surviving disease causing and food spoilage organisms may start to multiply again if the food is not properly handled. The disease-causing organisms in irradiated food are just as dangerous, but not more so, as the same organisms in non-irradiated food.

One concern has been that irradiation does not kill the bacteria that causes botulism. However, studies also have shown that in both irradiated and non-irradiated food, spoilage organisms will grow and alert consumers to spoilage before botulism-causing bacteria can produce toxin. Irradiation does produce chemical changes in foods. These substances, called "radiolytic products", may sound mysterious, but they are not. They have been scrutinized by scientists in making safety assessments of irradiated foods. Any kind of treatment causes chemical changes in food. For instance, heat treatment, or cooking, produces chemicals that could be called "thermolytic products." Scientists find the changes in food created by irradiation minor to those created by cooking. The products created by cooking are so significant that consumers can smell and taste them, whereas only a chemist with extremely sensitive lab equipment may be able to detect radiolytic products.

The use and transportation of radioactive materials, including the facilities in which they are used and the equipment in those facilities, is closely monitored by the Nuclear Regulatory Commission, state agencies and the Department of Transportation. The radioactive material itself is sealed within two layers of metal that prevent corrosion and oxidation. When shipped, it is placed within brick layers of lead that prevent gamma rays from escaping. Facilities must include many safety features to prevent both environmental and worker exposure. For example, when radioactive cobalt is in the storage position in an irradiator, it is under water and otherwise shielded. The irradiator is operated by remote control, and many other protections are required to prevent workers form entering the irradiation enclosure.

Until recently, only irradiated dried spices and enzymes were marketed in the United States. In January 1992, irradiated Florida strawberries were sold at a North Miami supermarket. Sales of irradiated products are on going in several grocery stores. Poultry irradiation began commercially in 1993. Irradiation of food has been approved in 37 countries for more than 40 products. The largest marketers of irradiated food are Belgium and France (each country irradiates about 10,000 tons of food per year), and the Netherlands (which irradiates bout 20,000 tons per year). Irradiated food cannot be recognized by sight, smell, taste, or feel. Irradiated foods will be labeled with a logo, along with the words Treated with Radiation or Treated by Irradiation [36].

Approximately 25% of all food products are lost after harvesting due to insects, vermin, and spoilage. Currently, a significant number of chemicals are used on food products for preserving/preventing insect losses. In roots and tubers, sprouting can be a major cause of losses. In developing countries where handling, transportation, and storage conditions are less adequate than in the United States these losses are significantly greater. In addition, foodborne diseases caused by pathogenic bacteria result in an estimated 9,000 deaths each year and 24 million cases of illness annually in the United States alone. Irradiation has the potential to significantly reduce both food production losses and foodborne illness.

X-rays - (machine generated), and gamma rays (occur naturally from radioactive decay of Cesium 137 or Cobalt 60). Cobalt-60 is most commonly used for food irradiation, though electron beam is finding increasing application. Currently, there are a number of nonfood related products being irradiated (cosmetics, wine corks, hospital supplies, medical products, packaging materials) mostly to achieve nonthermal sterilization. The radiation dose refers to the amount of these gamma rays absorbed by the product and is measured in Grays (Gy). 1 Gy = 1 Joule of absorbed energy / kg of product. Most treatment levels are on the order of 1 to 10 kGy (1 kGy = 1000 Gy). Because of the seriousness of the food safety issue and the lack of adequate control measures to ensure 100% bacteria free food, irradiation is seen as an additional tool that can be used for improving food safety. In particular, *E. coli*, salmonella, and a number of other pathogenic bacteria are sensitive to irradiation.

Hundreds of studies found no health-related issues from consuming irradiated food at levels less than 10 kGy. Some studies indicate that in irradiated pork the available thiamin may be reduced up to 50%. However, the average person would lose less than 2.3% of their thiamin intake eating irradiated pork, most comes from cereal grains (cereals, breads, and pastas). This is not an issue if one eats a well balanced diet. It is also important to note that in canned beef only 21% of the thiamin is retained compared to 23% retained for gamma irradiated beef, and 44% retained in electron irradiated beef. Other vitamin losses vary depending on the particular vitamin. A study comparing vitamin levels in irradiated and non-irradiated cooked poultry found comparable vitamin levels except a modest decrease in Vitamin E (35%) was noted. Vitamin losses can also be reduced by irradiating frozen products in vacuum-packed containers. Other studies suggest that vitamin losses in irradiated products can be reduced to l0% or less.

Ionizing radiation can also be used to produce sterile, shelf-stable products. Irradiation has been demonstrated to produce no harmful effects at levels up to and above 60 kGy. At these high levels, there have been some significant vitamin losses, but the product is commercially sterile and has a shelf-life comparable to canned foods. High levels of irradiation have already been approved for foods for NASA's Space Program and for immune compromised hospital patients. Irradiation can be used to sterilize (eliminate all microorganisms) food products at levels above 10 kGy. In the range of 1-10 kGy it can be used to pasteurize food (eliminate a significant number of microorganisms including those of public health significance). In some products it can be used as an insect disinfestation treatment (less than 1 kGy). It can be used as a sprout inhibition technique in potatoes and onions (less than 0.5 kGy). It can delay ripening of certain fruits (less than 0.3 kGy) and eliminate trichinosis in pork (less than 1.0 kGy).

Silicate minerals contaminating foodstuffs store energy by charge trapping processes as a result of exposure to ionizing radiation. Releasing such energy, by controlled heating of isolated silicate minerals, gives rise to measurable TL glow curves. Silicate minerals are therefore isolated from the foodstuffs, mostly by a density separation step. In order not to obscure the TL, the isolated silicate minerals should be as free of organic constituents as possible. A first glow of the separated mineral extracts is recorded.

Since various amounts and/or types of minerals (quartz, feldspar etc.) exhibit very variable integrated TL intensities after irradiation, a second TL glow (Glow 2) of the same sample after exposure to a fixed dose of radiation is necessary to normalize the TL response. The TL glow ratio, thus obtained, is used to indicate radiation treatment of the food, since the population of irradiated samples on principle yields higher TL glow ratios than that of unirradiated samples. Glow shape parameters offer additional evidence for identifying irradiated foods. This method of TL analysis relies solely on the silicate minerals which can be separated from various foods and is not principally influenced by the kind of food product.

2.2. Basic concepts of thermoluminescence in solids

TLD is based on materials which (after exposure to ionizing radiation) emit light while they are heated. The impurities in the TL material give rise to localized energy levels within the forbidden energy band gap and that these are crucial to the TL process. As a means of detecting the presence of these defect levels, the sensitivity of TL is unrivalled. Townsend and Kelly [37] estimate that the technique is capable of detecting as few as 10^9 defects levels in a specimen. To put this number into perspective one should realize that detectable chemical `purity' in a sample is six orders of magnitude higher. The high sensitivity, allows the determination of very low radiation doses. On the other hand, it handicappes us in investigation into the relation between the luminescence and the defects involved in this process. The sensitivity of thermoluminescent material varies depending on the type of dosimeter.

TL is a luminescence phenomenon of an insulator or semiconductor which can be observed when the solid is thermally stimulated. TL should not be confused with the light spontaneously emitted from a substance when it is heated to incandescence. At higher temperatures (say in excess of 200°C) a solid emits (infra) red radiation of which the intensity increases with increasing temperature. This is thermal or black body radiation. TL, however, is the thermally stimulated emission of light following the previous absorption of energy from radiation. According to this phenomenon, the three essential ingredients necessary for the production of TL can be deduced. Firstly, the material must be an insulator or semiconductor–metals do not exhibit luminescent properties.

Secondly, the material must have at some time absorbed energy during exposure to ionizing radiation. Thirdly, the luminescence emission is triggered by heating the material [38]. A thermoluminescent material is a material that absorbs some energy which is stored during exposure to ionizing radiation. When the material is heated, the stored energy is released in the form of visible light as seen in Fig.2.1. In fact that TL does not refer to thermal *excitation*, but to *stimulation* of luminescence in a sample which was excited in a different way. TL material can not emit light again by simply cooling the sample and reheating it another time. It should first be re-exposed to ionizing radiation before it produces light again. The storage capacity of a TL material makes it suitable for dosimetric applications.

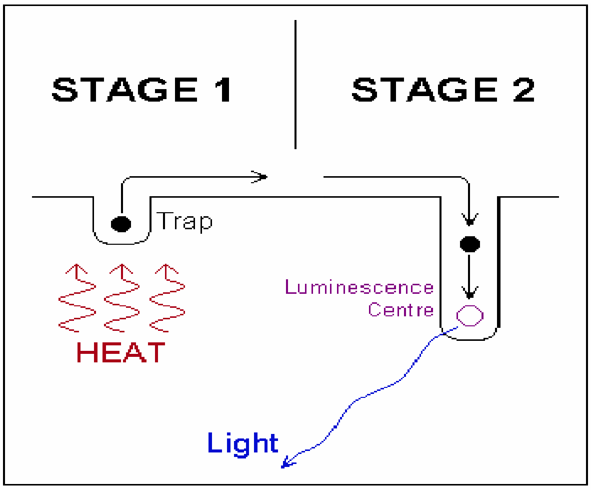

Figure 2.1. Phenomena of thermal excitation of luminescence

2.3. The one trap–one centre model

The energy band theory of solids explains the observed TL properties. In an ideal semiconductor or insulator crystalline most of the electrons reside in the valence band. The next highest band that the electrons can occupy is the conduction band, separated from the valence band by the so-called forbidden band gap. The energy difference between the valence band and conduction band is E_g. However, whenever structural defects occur in a crystal, or if there are impurities within the lattice, there is a possibility for electrons to possess energies which are forbidden in the perfect crystal. In a simple TL model two levels are assumed, one situated below the bottom of the conduction band and the other situated above the top of the valence band (Fig. 2.2). The highest level indicated by T is situated above the equilibrium Fermi level (E_f) and thus empty in the equilibrium state, i.e. before the exposure to radiation and the creation of electrons and holes. It is therefore a potential electron trap. The other level (indicated by R) is a potential hole trap and can function as a recombination centre.

The absorption of radiant energy with $h\nu > E_g$ results in ionisation of valence electrons, producing energetic electrons and holes which will, after thermalization, produce free electrons in the conduction band and free holes in the valence band (transition a). The free charge carriers recombine with each other or become trapped. In the case of direct recombination an amount of energy will be released which may excite a luminescent centre.

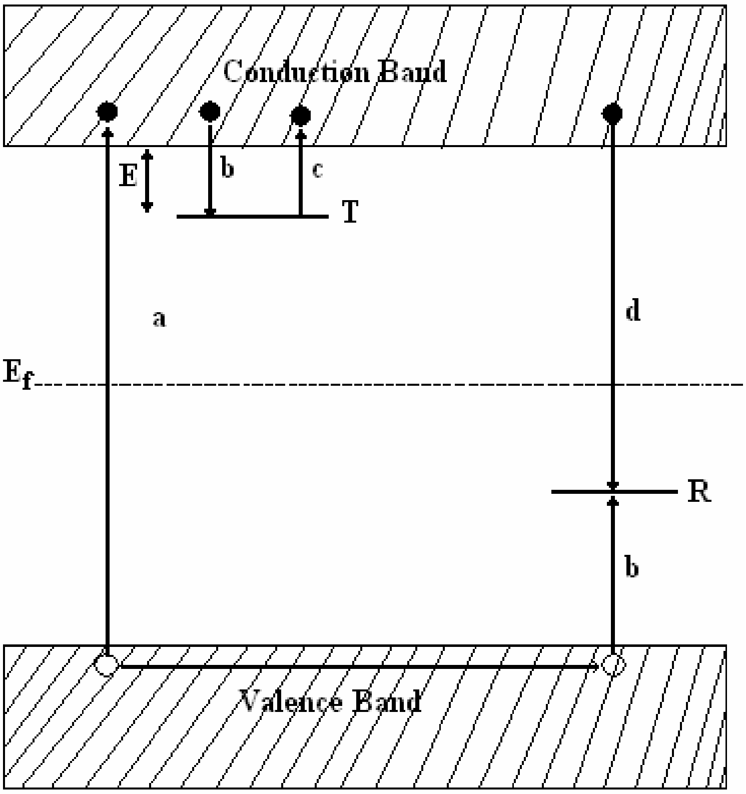

Figure 2.2. Energy band model showing the electronic transitions in a TL material according to a simple two-level model (a) generation of electrons and holes; (b) electron and hole trapping; (c) electron release due to thermal stimulation; (d) recombination. (●) shows electrons, (○) shows holes. Level T is an electron trap, level R is a recombination centre, E_f is Fermi level

The luminescent centre relaxes (returns to the ground state) under the emission of light. However, in semiconductors and insulators a certain percentage of the charge carriers is trapped: the electrons at T and the holes at R (transition b). The probability per unit time of release of an electron from the trap is assumed to be described by the Arrhenius equation,

$$p = s \exp\left\{ -\frac{E}{kT} \right\} \tag{2.1}$$

where p is the probability per unit time, s is the frequency factor [39]. In the simple model s is constant, E is called the trap depth or activation energy, the energy needed to release an electron from the trap into the conduction band (see Fig.2.2).

The other symbols have their usual meaning: k is Boltzmann's constant = 8.617×10^{-5} eV/K, and T is the absolute temperature. If the trap depth $E >> kT_0$, with T_0 the temperature at irradiation, trapped electrons will remain for a long period of time, until exposure to the radiation there will exist a substantial population of trapped electrons. There must be an equal population of trapped holes at level R, due to the free electrons and holes created and annihilated in pairs. Because the normal equilibrium Fermi level E_f is situated below level T and above level R, these populations of trapped electrons and holes represent a non-equilibrium state. The reaction path for return to equilibrium is always open, but because the perturbation from equilibrium (during exposure to ionising radiation) was performed at low temperature (compared to E/k), the relaxation rate as determined by Eqn. 2.1 is slow. Thus, the non-equilibrium state is metastable and will exist for an indefinite period, governed by the rate parameters E and s.

The return to equilibrium can be speeded up by raising the temperature of the TL material above T_0. This will increase the probability of detrapping and the electrons will now be released from the trap into the conduction band. The charge carrier migrates through the conduction band of the crystal until it undergoes recombination at recombination centre R. In the simple model this recombination centre is a luminescent centre where the recombination of the electron and hole leaves the centre in one of the higher excited states. Return to the ground state is coupled with the emission of light quanta, i.e. TL. The intensity of TL in photons $I(t)$ per second at any time t during heating is proportional to the rate of recombination of holes and electrons at R. If m (m^{-3}) is the concentration of holes trapped at R the TL intensity can be written as

$$I(t) = -\frac{dm}{dt} \tag{2.2}$$

Here we assume that each recombination produces a photon and that all produced photons are detected. The rate of recombination will be proportional to the concentration of free electrons in the conduction band n_c and the concentration of holes m,

$$I(t) = -\frac{dm}{dt} = n_c m A \tag{2.3-a}$$

with the constant A the recombination probability expressed in units of volume per unit time which is assumed to be independent of the temperature. The rate of change of the concentration of trapped electrons n is equal to the rate of thermal release minus the rate of retrapping,

$$-\frac{dn}{dt} = np - n_c(N-n)A_r \tag{2.3-b}$$

with N the concentration of electron traps and A_r the probability of retrapping (m^3/s). Likewise the rate concentration of free electrons is equal to the rate of thermal release minus the rate of retrapping and the rate of recombination,

$$\frac{dn_c}{dt} = np - n_c(N-n)A_r - n_c m A \tag{2.3-c}$$

Eqn.(2.3a)-(2.3c) described the charge carrier traffic in the case of release of a trapped electron from a single-electron trap and recombination in a single centre. For TL produced by the release of holes the rate equations are similar to Eqn.(2.3a)-(2.3c). These equations form the basis of many analyses of TL phenomena. There is no general analytical solution. To develop an analytical expression some simplifying assumptions must be made. An important assumption is at any time

$$\left|\frac{dn_c}{dt}\right| << \left|\frac{dn}{dt}\right|, \qquad \left|\frac{dn_c}{dt}\right| << \left|\frac{dm}{dt}\right| \tag{2.4}$$

This assumption is called by Chen and McKeever [39] the quasiequilibrium assumption since it requires that the free electron concentration in the conduction band is quasistationary. The trapped electrons and holes are produced in pairs during the irradiation. Charge neutrality dictates therefore

$$n_c + n = m \tag{2.5}$$

which for $n_c \approx 0$ means that $n \approx m$ and

$$I(t) = -\frac{dm}{dt} \approx -\frac{dn}{dt} \tag{2.6}$$

Since $dn_c/dt \approx 0$ one gets from (2.3a) and (2.3b):

$$I(t) = \frac{mAns \exp\left\{-\frac{E}{kT}\right\}}{(N-n)A_r + mA} \tag{2.7}$$

2.3.1. First-order kinetics

Even Eqn.(2.7) cannot be solved analytically without additional simplifying assumptions. Randall and Wilkins [40-41] assumed negligible retrapping during the heating stage, i.e. they assumed $mA >> (N-n)A_r$. Under this assumption Eqn.(2.7) can be written

$$I(t) = -\frac{dn}{dt} = sn \exp\left\{-\frac{E}{kT}\right\} \tag{2.8}$$

This differential equation describes the charge transport in the lattice as a first-order process and the glow peaks calculated from this equation are called first-order glow peaks. Solving the differential Eqn.(2.8) yields

$$I(t) = -\frac{dn}{dt} = n_o s \exp\left\{-\frac{E}{kT}\right\} \exp\left\{-s\int_0^t \exp\left\{-\frac{E}{kT(t')}\right\} dt'\right\} \tag{2.9}$$

where n_0 is the total number of trapped electrons at time t=0. Usually the temperature is raised as a linear function of time according to

$$T(t) = T_o + \beta t \tag{2.10}$$

with β the constant heating rate and T_0 the temperature at t=0. This gives for the intensity as function of temperature

$$I(T) = -\frac{1}{\beta}\frac{dn}{dt} = n_o \frac{s}{\beta}\exp\left\{-\frac{E}{kT}\right\}\exp\left\{-\frac{s}{\beta}\int_{T_o}^{T}\exp\left\{-\frac{E}{kT'}\right\}dT'\right\} \tag{2.11}$$

This is the well-known Randall–Wilkins first-order expression of a single glow peak. The peak has a characteristic asymmetric shape being wider on the low temperature side than on the high temperature side. On the low temperature side, i.e. in the initial rise of the glow peak, the intensity is dominated by the first exponential ($\exp(-E/kT)$). Thus, if I is plotted as function of $1/T$, a straight line is expected in the initial rise temperature range, with the slope of $-E/k$, from which the activation energy E is readily found.

The properties of the Randall–Wilkins equation are illustrated in Fig.2.3. In Fig.2.3(a) it is shown how $I(T)$ varies if n_0 varies from $n_0=0.25$ m^{-3} till $n_0=2$ m^{-3} while $E=1$ eV, $s=1.0\times10^{12}$ s^{-1} and $\beta=1$ K/s are kept constant. It can be noted that the temperature at the peak maximum, T_m, stays fixed. This is a characteristic of all first-order TL curves. The condition for the maximum can be found by setting $dI/dt=0$ (or, somewhat easier from $d\ln I(T)/dt=0$). From this condition one gets

$$\frac{\beta E}{kT_m^2} = s\exp\left\{-\frac{E}{kT_m}\right\} \tag{2.12}$$

In this equation n_0 does not appear which shows that T_m does not depend on n_0. From Fig.2.3(a) it can be further seen that not only the peak height at the maximum but each point of the curve is proportional to n_0. In the application in dosimetry n_0 is the parameter of paramount importance since this parameter is proportional to the absorbed dose. It is simple to see that the area under the glow peak is equal to n_0 since

$$\int_0^\infty I(t)dt = -\int_0^\infty \frac{dn}{dt}dt = -\int_{n_0}^{n_\infty} dn = n_0 - n_\infty \tag{2.13}$$

and n_∞ is zero for $t\rightarrow\infty$. In Fig.2.3(b) the activation energy E has been varied from 0.8 to 1.2 eV. As E increases the peak shifts to higher temperatures with a decrease in the height and an increase in the width keeping the area (i.e. n_0) constant.

Similar changes can be noticed as s is varied (see Fig.2.3(c)) but now in the opposite way: as s increases the peak shifts to lower temperatures with an increase of the height and a decrease in width. In Fig.2.3(d) the heating rate has been varied. As β increases the peak shifts to higher temperatures while the height decreases and the width increases just as in the case of decreasing s. This can be expected since s and β appear as a ratio s/β in Eqn.(2.11).

It is worthwhile to note that of the four parameters the activation energy E and the frequency factor s are the main physical parameters. They are called the trapping parameters and are fixed by the properties of the trapping centre. The other two parameters can be chosen by the experimenter by choosing a certain dose (n_0) and by read-out of the signal at a certain heating rate β. Investigation of a new TL material will therefore start with studying the glow peak behaviour under variation of the absorbed dose and the heating rate.

The evaluation of Eqn.(2.11) is hampered by the fact that the integral on the right-hand side is not elementary in the case of linear heating. Chen [42] has shown how the integral can be approximated by asymptotic series. In practical applications it is convenient to describe the glow peak in terms of parameters which are easy to derive experimentally, namely the intensity of peak at the maximum I_m and the temperature at the maximum T_m. Kitis et al. [43] have shown that Eqn.(2.11) can be quite accurately approximated by

$$I(T) = I_m \exp\left[1 + \frac{E}{kT}\frac{T - T_m}{T_m} - \frac{T^2}{T_m^2}\exp\left\{\frac{E}{kT}\frac{T - T_m}{T_m}\right\}(1 - \Delta) - \Delta_m\right] \tag{2.14}$$

with $\Delta=2kT/E$ and $\Delta_m=2kT_m/E$. Recently Pagonis et al.[44] have shown that a Weibull distribution function also accurately describes the first-order TL curve. These expressions may be convenient for peak fitting purposes.

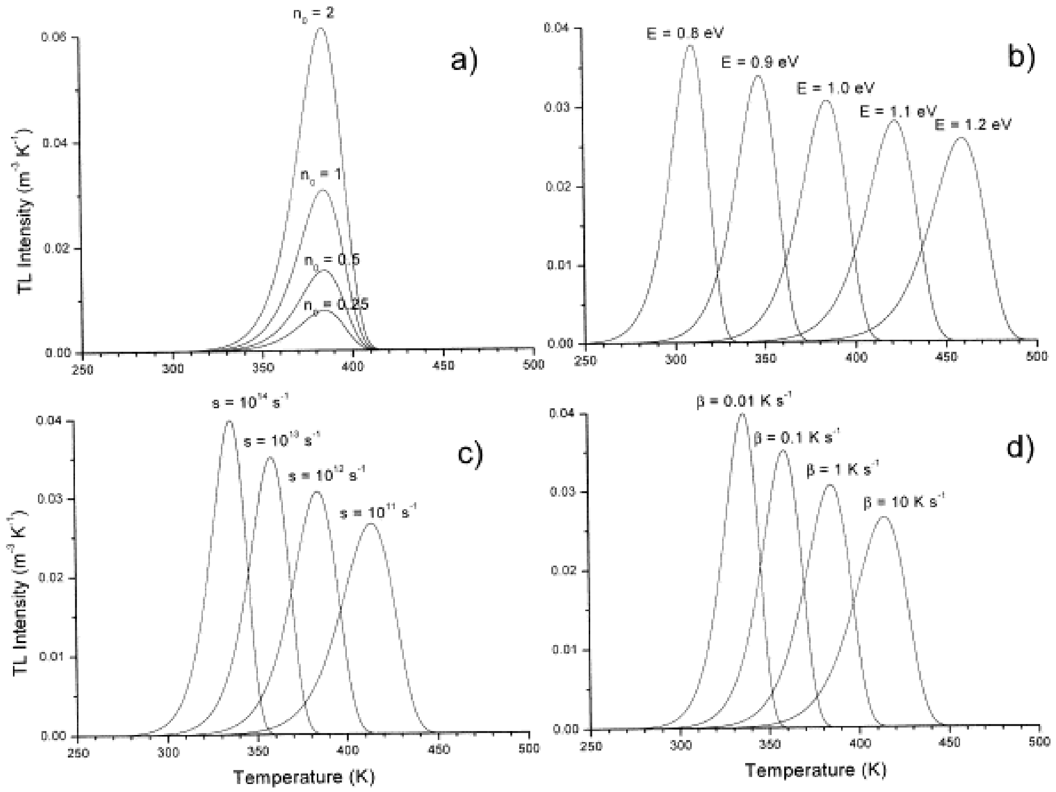

Figure 2.3: Properties of the R–W first-order TL equation, showing: (a) variation with n_0, the concentration of trapped charge carriers after irradiation; (b) the variation with E, the activation energy; (c) the variation with s, the escape frequency; (d) the variation with β, the heating rate. Parameter values: $n_0=1$ m^{-3}; $E=1$ eV; $s=1\times10^{12}$ s^{-1}, $\beta=1$ K/s of which one parameter is varied while the others are kept constant

2.3.2. Second-order kinetics

Garlick and Gibson [45] considered the possibility that retrapping dominates, i.e. $mA \ll (N-n)A_r$. Further they assume that the trap is far from saturation, i.e. $N \gg n$ and $n=m$. With these assumptions, Eqn.(2.7) becomes

$$I(t) = -\frac{dn}{dt} = s\frac{A}{NA_r}n^2\exp\left\{-\frac{E}{kT}\right\} \tag{2.15}$$

We see that now dn/dt is proportional to n^2 which means a second-order reaction. With the additional assumption of equal probabilities of recombination and retrapping, $A=A_r$, integration of Eqn.(2.15) gives

$$I(T) = \frac{n_0^2}{N}\frac{s}{\beta}\exp\left\{-\frac{E}{kT}\right\}\left[1+\frac{n_0 s}{N\beta}\int_{T_0}^{T}\exp\left\{-\frac{E}{kT'}\right\}dT'\right]^{-2} \tag{2.16}$$

This is the Garlick–Gibson TL equation for second-order kinetics. The main feature of this curve is that it is nearly symmetric, with the high temperature half of the curve slightly broader than the low temperature half. This can be understood from the consideration of the fact that in a second-order reaction significant concentrations of released electrons are retrapped before they recombine, in this way giving rise to a delay in the luminescence emission and spreading out of the emission over a wider temperature range.

The initial concentration n_0 appears here not merely as a multiplicative constant as in the first-order case, so that its variation at different dose levels change the shape of the whole curve. This is illustrated in Fig.2.4(a). It is seen that T_m decreases as n_0 increases. It can be derived [46] that the temperature shift can be approximated by

$$T_1 - T_2 \approx T_1 T_2 \frac{k}{E} \ln f \tag{2.17}$$

where T_1 is the temperature of maximum intensity at a certain dose and T_2 the temperature of maximum intensity at f times higher dose. With the parameter values of Fig.2.4(a) the shift is 25 K. When E=1 eV, T_1=400 K and the absorbed dose is increased by a factor 1000, which is easy to realise experimentally, a temperature shift of 77 K can be expected.

From Eqn.(2.17) it follows further that for a given increase of the dose the shallower the trap, i.e., the smaller E, the larger the peak shift. Fig.2.4(b) illustrates the variation in size and position of a second-order peak as function of E, in Fig.2.4(c) s function of s/N, and in Fig.2.4(d) as function of the heating rate. The area under the curve is, as in the case of first-order kinetics, proportional to the initial concentration n_0 but the peak height is no longer directly proportional to the peak area, although the deviation is small.

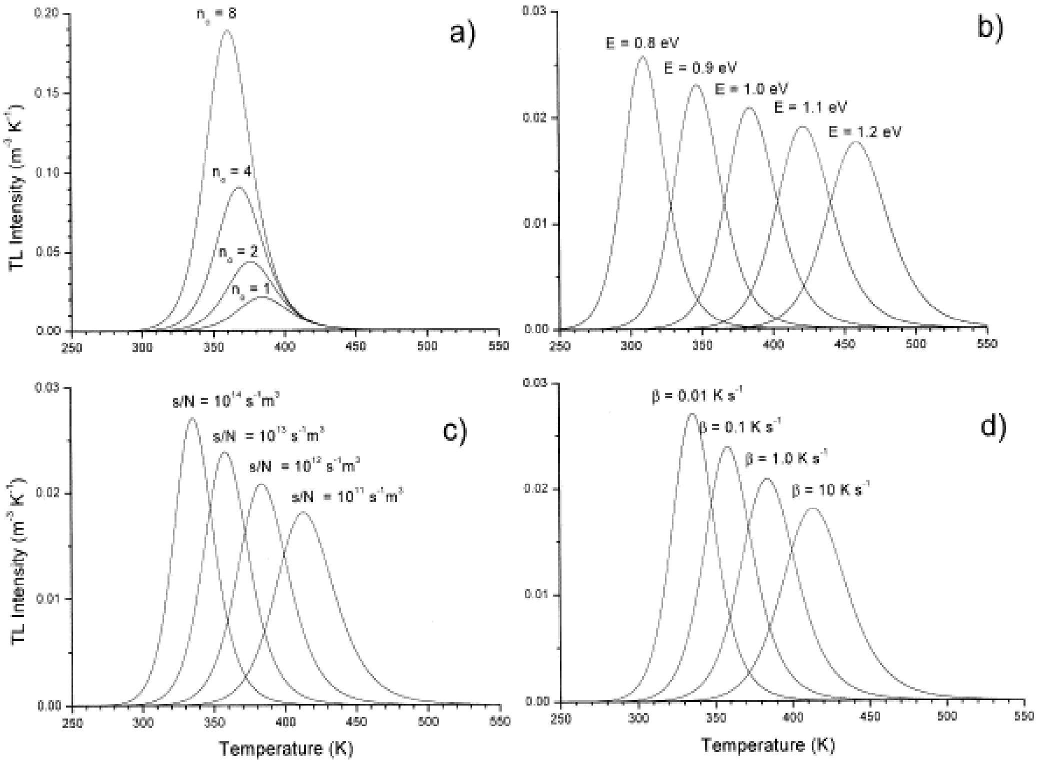

Figure 2.4. Properties of the Garlick–Gibson second-order TL equation, showing: (a) variation with n_0, the concentration of trapped charge carriers after irradiation; (b) the variation with E, the activation energy; (c) the variation with s/N; (d) the variation with β, the heating rate. Parameter values: n_0=1 m^{-3}; E=1 eV; s/N=1×10^{12} s^{-1} m^3, β=1 K/s of which one parameter is varied while the others are kept constant

Note that, similarly to the first-order case, the term dominating the temperature dependence in the initial rise is exp(-E/kT). So the `initial rise method' for the determination of the trap depth can be applied here as well.

Also for second-order kinetics the glow peak shape, Eqn.(2.16) can be approximated with a function written in terms of maximum peak intensity I_m and the maximum peak temperature T_m [34]

$$I(T) = 4I_m \exp(\frac{E}{kT}\frac{T-T_m}{T_m}) \times \left[\frac{T^2}{T_m^2}(1-\Delta)\exp\left\{\frac{E}{kT}\frac{T-T_m}{T_m}\right\} + 1 + \Delta_m\right]^{-2} \qquad (2.18)$$

with Δ and Δ_m the same meaning as in Eqn.(2.14).

2.3.3. General-order kinetics

The first- and second-order forms of the TL equation have been derived with the use of specific, simplifying assumptions. However, when these simplifying assumptions do not hold, the TL peak will fit neither first- nor the second-order kinetics. May and Partridge [47] used for this case an empirical expression for general-order TL kinetics, namely

$$I(t) = -\frac{dn}{dt} = n^b s' \exp\left\{-\frac{E}{kT}\right\} \tag{2.19}$$

where s' has the dimension of $m^{3(b-1)}$ s^{-1} and b is defined as the general-order parameter and is not necessarily 1 or 2. Integration of Eqn.(2.19) for $b \neq 1$ yields

$$I(T) = \frac{s''}{\beta} n_0 \exp\left\{-\frac{E}{kT}\right\}\left[1 + (b-1)\frac{s''}{\beta}\int_{T_0}^{T} \exp\left\{-\frac{E}{kT'}\right\}dT'\right]^{-b/(b-1)} \tag{2.20}$$

where now $s'' = s' n_0^{b-1}$ with unit s^{-1}. Eqn.(2.20) includes the second-order case (b=2) and reduces to Eqn.(2.11) when $b \to 1$. It should be noted that according to Eqn.(2.19) the dimension of s' should be $m^{3(b-1)}$ s^{-1} that means that the dimension changes with the order b which makes it difficult to interpret physically. Still, the general-order case is useful since intermediate cases can be dealt with and it smoothly goes to first- and second-orders when $b \to 1$ and $b \to 2$, respectively (see Fig.2.5).

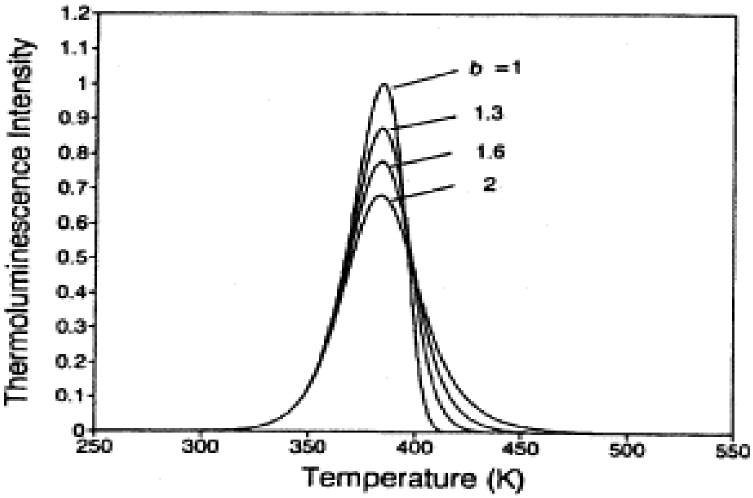

Figure 2.5. Comparison of first-order (b=1), second-order (b=2) and intermediate-order (b=1.3 and 1.6) TL peaks, with E=1 eV, $s=1\times10^{12}$ s^{-1}, $n_0=N$=1 m^{-3} and β=1 K/s (from [34]).

2.3.4 Advanced models

The one trap–one centre model shows all the characteristics of the phenomenon TL and explains the behaviour of the glow peak shape under variation of the dose and heating rate. However, there is no existing TL material known that accurately is described by the simple model.

This does not mean that the simple model has no meaning. On the contrary, it can help us in the interpretation of many features which can be considered as variations of the one trap–one centre model. There is no room to discuss all the advanced (more realistic) models in detail. The text book of Chen and McKeever [39] for a deeper and quantitative treatment is referred. Here, only some models are very briefly mentioned in order to get some idea about the complexity of the phenomenon in a real TL material.

In general, a real TL material will show more than one single electron trap. Not all the traps will be active in the temperature range in which the specimen is heated. A thermally disconnected trap is one which can be filled with electrons during irradiation but which has a trap depth which is much greater than the active trap such that when the specimen is heated only electrons trapped in the active trap (AT) and the shallow trap (ST) (see Fig.2.6(a)) are freed. Electrons trapped in the deeper levels are unaffected and thus this deep electron trap (indicted in Fig.2.6(a) with DET) is said to be thermally disconnected. But its existence has a bearing on the trapping filling and eventually on the shape of the glow peak [48].

In Section 2.1 it was assumed that the trapped electrons are released during heating while the trapped holes are stable in the recombination centre. A description in which the holes are released and recombine at a centre where the electrons are stable during heating is mathematically identical. However, the situation will change if both electrons and holes are released from their traps at the same time at the same temperature interval and the holes are being thermally released from the same centres as are acting as recombination sites for the thermally released electrons and vice versa (see Fig.2.6(b)). In this case Eqn.(2.2) is no longer valid. New differential equations should be drafted. Analysis of this complicated kinetic model reveals a TL glow curve which retains the simple Randall–Wilkins (Eqn.(2.11)) or Garlick–Gibson (Eqn.(2.16)) shape, depending upon the chosen values of the parameters. However, the *E* and *s* values used in Eqn.(2.11) and Eqn.(2.16) in order to obtain a fit on this complicated kinetic model need further interpretation.

Another process which might happen is a recombination without a transition of the electron into the conduction band (Fig.2.6(c)) Here the electron is thermally stimulated into an excited state from which a transition into the recombination centre is allowed. This means that the trap has to be in the proximity of a centre.

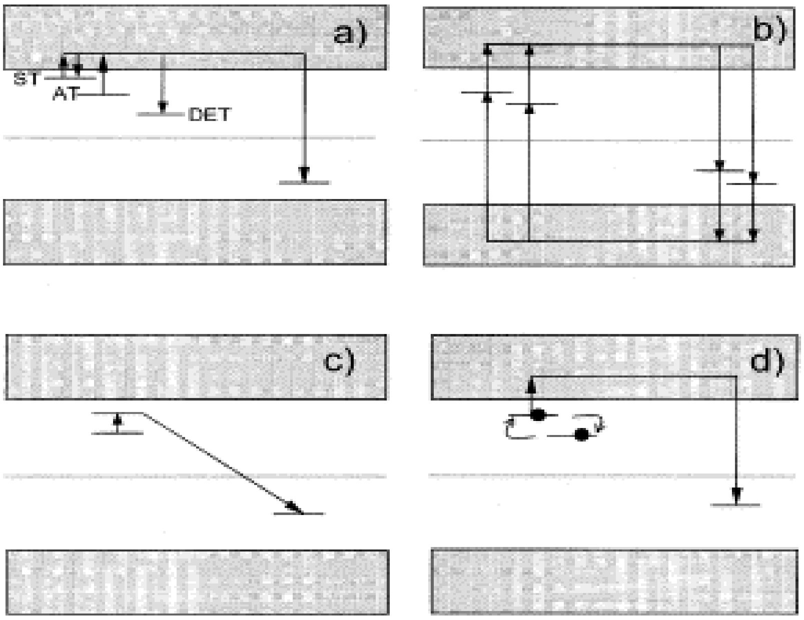

Figure 2.6. Advanced models describing the thermally stimulated release of trapped charged carriers including: (a) a shallow trap (ST), a deep electron trap (DET), and a active trap (AT); (b) two active traps and two recombination centres; (c) localised transitions; (d) defect interaction (trapping centre interacts with another defect).

The transition probability may strongly depend on the distance between the two centres. Under certain assumptions an expression for the TL intensity can be derived [49] which has the same form as Eqn.(2.11) but with *s* replaced by a quantity related to the probability for recombination. This means that these localised transitions are governed by first-order kinetics.

Finally, we will mention the possibility that the defect which has trapped the electron is not stable but is involved in a reaction with another defect (Fig.2.6(d)). The result may be that at low temperature the trap depth is changing while the trapped electron concentration is stable. At higher temperatures electrons are involved in two processes: the escape to the conduction band and the defect reaction. Piters and Bos [50] have defect reactions incorporated into the rate equations and glow curves simulated. It appears that the simulated glow curves can be very well fitted by Eqn.(2.11). It is clear that (again) the fitting parameters do not have the simple meaning of trap depth and escape frequency.

2.4. Trapping Parameter Determination Methods

The determination of trapping parameters from thermoluminescence glow curves has been a subject of interest for half a century. There are various methods for evaluating the trapping parameters from the glow curves [40-41, 49, 51-55].

When one glow peak is highly isolated from the others, the experimental methods such as initial rise, variable heating rates, isothermally decay, and peak shape methods are suitable methods to determine these parameters. However in most materials, the glow curve consists of several peaks as in the APSQ. In case of overlapping peaks there are essentially two ways to obtain these parameters, the first one is the partial thermal cleaning method and the second one is the computer glow curve deconvolution program. In most cases, the partial thermal cleaning method can not be used to completely isolate the peak of interest without any perturbation on it. Therefore, the computer glow curve deconvolution program has become very popular method to evaluate trapping parameters from TL glow curves in recent years [56].

2.4.1 Peak Shape Method

Evaluation of E from the shape of the peak utilising parameters such as T_m , full width at half-maximum $\omega=T_2-T_1$, half width on the high temperature side of the maximum $\delta = T_2 - T_m$, half width on the low-temperature side of the maximum $\tau = T_m - T_1$, and $\mu_g = \delta/\omega$ called the shape parameter.

The order of kinetics b can be estimated by means of shape parameters. Chen [42] found that μ_g is not sensitive to changes in E and s, but it changes with the order of kinetics b. It has been shown that the ranges of μ_g varies from 0.42 for b=1 to 0.52 for b=2 in case of linear heating.

The first peak shape method was developed by Grossweiner [52]; later Chen [42] modified Halperin and Braner's equations [53] for calculating E values;

$$
\begin{aligned}
E_\tau &= \left[1.51 + 3(\mu_g - 0.42)\right]\frac{kT_m^2}{\tau} - \left[1.58 + 4.2(\mu_g - 0.42)\right]2kT_m \\
E_\delta &= \left[0.976 + 7.3(\mu_g - 0.42)\right]\frac{kT_m^2}{\delta} \\
E_\omega &= \left[2.52 + 10.2(\mu_g - 0.42)\right]\frac{kT_m^2}{\omega} - 2kT_m
\end{aligned}
\tag{2.21}
$$

After determination of the activation energy and the order of kinetics, using the following expressions the frequency factor s, it must be noted that this parameter called as pre-exponential factor in the general order kinetic, can be estimated for first and general order kinetics respectively.

$$
\begin{aligned}
s &= \frac{\beta E}{kT_m^2}\exp\left[\frac{E}{kT_m}\right] \\
s &= \frac{\beta E}{kT_m^2}\left[\exp(-\frac{E}{kT_m})(1 + (b-1)\frac{2kT_m}{E})\right]^{\frac{b}{b-1}}
\end{aligned}
\tag{2.22}
$$

2.4.2 Isothermal Decay Method

The isothermal decay is quite a different method of analysis of the trapping parameters in which the TL sample temperature is kept constant and the light emission can be recorded as a function of time. Generally, in the isothermal decay method, the following equation is solved for constant T for the first order kinetics

$$I(T) = -c\frac{dn}{dt} = c\frac{n_0}{\tau}\exp(-\frac{t}{\tau}) \tag{2.23}$$

where n_0 is the initial value of n and $\tau = s^{-1}\exp(\frac{E}{kT})$.

The above equation shows that at a constant temperature T, the light emission will decay exponentially with time t and a plot of $ln(I)$ against t will give a straight line with a slope $m = s\exp(-\frac{E}{kT})$. In order to find E and s, the experiments are carried out at two different constant temperatures T_1 and T_2, resulting in two different slopes m_1 and m_2. Thus the activation energy can be determined by using the following equation

$$E = \frac{k}{(\frac{1}{T_2} - \frac{1}{T_1})}\ln(\frac{m_1}{m_2}) \tag{2.24}$$

The isothermal decay method is not applicable to higher order kinetics. In 1979; a method has been proposed by Kathuria and Sunta [57] to calculate the order of kinetics from the isothermal decay of thermoluminescence. According to this method; if the decaying intensity from the sample is held at a constant temperature, the plot of $I^{(\frac{1}{b}-1)}$ versus t gives a straight line, when the proper value of b is chosen. Therefore, various b values are tried and the correct one is that giving a straight line.

2.4.3 CGCD Method

Computer Glow Curve Deconvolution (CGCD) is one of the most important method to determine trapping parameters from TL glow curves. This method has the advantage over experimental methods in that they can be used in largely overlapping-peak glow curves without resorting to heat treatment

In this study, a CGCD program was used to analyse the glow curve of APSQ. The program was developed at the Reactor Institute at Delft, The Netherlands [58]. This program is capable of simultaneously deconvoluting as many as nine glow peaks from glow curve. Two different models were used in the computer program. In the first model, the glow curve is approximated from first order TL kinetic by the expression,

$$I(T) = n_0 s \quad \exp(-\frac{E}{kT})\exp\left[(-\frac{s\ kT^2}{\beta\ E}\exp(-\frac{E}{kT}) * (0.9920 - 1.620\frac{kT}{E_a})\right] \qquad (2.25)$$

In the second model the glow curve is approximated with general order TL kinetics by using the expression,

$$I(T) = n_0 s \quad \exp(-\frac{E}{kT})\left[1 + (-\frac{(b-1)s\ kT^2}{\beta \quad E}\exp(-\frac{E}{kT}) * (0.9920 - 1.620\frac{kT}{E_a})\right]^{\frac{b}{b-1}} \qquad (2.26)$$

where n_0 (m^{-3}) is the concentration of trapped electrons at t=0, s (s^{-1}) is the frequency factor for first-order and the pre-exponential factor for the general-order, E (eV) the activation energy, T (K) the absolute temperature, k (eVK^{-1}) Boltzmann's constant, β ($^0Cs^{-1}$) heating rate and b the kinetic order.

The summation of overall peaks and background contribution can lead to composite glow curve formula as shown below

$$I(T) = \sum_{i=1}^{n} I_i(T) + a + b\exp(T) \qquad (2.27)$$

where $I(T)$ is the fitted total glow curve, a allows for the electronic noise contribution to the planchet and dosimeters infrared contribution to the background.

Starting from the above Eqn.(2.27), the least square minimisation procedure and also FOM (Figure of Merit) was used to judge the fitting results as to whether they are good or not. i.e.

$$FOM = \sum_{i=1}^{n}\frac{|N_i(T) - I(T)|}{A} = \sum_{i=1}^{n}\frac{|\Delta N_i|}{A} \qquad (2.28)$$

where $N_i(T)$ is the i-th experimental points (total n=200 data points), $I(T)$ is the i-th fitted points, and A is the integrated area of the fitted glow curve.

From many experiences [59-60], it can be said that if the values of the FOM are between 0.0% and 2.5% the fit is good, 2.5 % and 3.5% the fit is fair, and > 3.5% it is bad fit.

To have a graphic representation of the agreement between the experimental and fitted glow curves, the computer program also plots the function,

$$X(T) = \frac{N_i(T) - I_i(T)}{\sqrt{I_i(T)}} \tag{2.29}$$

which is a normal variable with an expected value 0 and σ=1 where $\sigma^2(T)=I_i(T)$.

2.4.4.Initial Rise Method

The simplest, and most generally applicable method for evaluating the activation energy E of a single TL peak is the initial rise method. The basic premise upon which this method is based is that at the low temperature end of the peak,all the relevant occupancies of the states, the trap, the recombination center and, in some cases, other interactive states can be considered as being approximately constant.

The rise of the measured intensity as a function of temperature in this region is, therefore, very close to exponential, thus

$$I(T) = C\exp(-E/kT) \tag{2.30}$$

where the constant C includes all the dependencies on the other parameters and occupancies, E is the activation energy (eV), k is the Boltzmann`s constant (eV/K^{-1}) and T is the temperature (K).

Plotting ln(I) against $1/T$ a linear plot is obtained with slope equal to $-E/k$. Hence it is possible to evaluate E without any knowledge of the frequency factor s by means of equation

$$E = -kd(\ln(I))/d(1/T) \tag{2.31}$$

Once the value of E was determined, the frequency factor (s) was obtained from the equation

$$\frac{\beta E}{kT_m} = s\exp(-\frac{E}{kT}) \tag{2.32}$$

where T_m is the temperature at the maximum intensity. This method can only be used when the glow peak is well defined and clearly seperated from the other peaks.

2.4.5.Heating Rate Method

Another important method is various heating rates for the determination of activation energies. If a sample is heated at two different linear heating rates β_1 and β_2 the peak temperatures will be different. Equation (2.32) can therefore, be written for each heating rate and dividing the equation for β_1 (and T_{m1}) by the equation for β_2 (and T_{m2}) and rearranging, one gets an explicit equation for the calculation of E

$$E = k\frac{T_{m1}T_{m2}}{T_{m1}-T_{m2}}\ln[(\frac{\beta_1}{\beta_2})(\frac{T_{m2}}{T_{m1}})^2] \tag{2.33}$$

The major advantage of the heating rate method is that it only requires data to be taken at a peak maximum (T_m, I_m) which, in case of a large peak surrounded by smaller satellites, can be reasonably accurately determined from the glow curve. Furthermore the calculation of E is not affected by problems due to thermal quenching, as with the initial rise method.

When various heating rates for the first-order kinetics are used, the following expression is obtained:

$$\ln(\frac{T_m^2}{\beta}) = (\frac{E}{k})(\frac{1}{Tm}) + cons\tan t \tag{2.34}$$

A plot of ln (T_m^2/β)versus ($1/ T_m$) should yield a straight line with a slope E/k, then E is found. Additionally, extrapolating to $1/T_m =0$, a value for $ln(sk/E)$ is obtained from which s can be calculated by inserting the value of E/k found from the slope. This method of various heating rates are applicable for general-order kinetics which includes the second-order case. For the general order case, one can plot $ln\left[I_m^{b-1}(T_m^2/\beta)^b\right]$ versus $1/T_m$, whose slope is equal to E/k.

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 Material and Method

Two types of dried legumes (corn and chickpea) were purchased from the local market of Gaziantep. Seperation of the organic and inorganic phases was used carbon tetrachloride ($CCI_{4;}$; Raftel, Turkey), hydrogen peroxide (H_2O_2; Merck, Germany) and sodium hypochlorite (NaCIO; Merck, Germany).

Samples of chickpea and corn were acquired at random from commercial sources in Turkey, without knowing the producer. Since the food irradiation technology for commercial food processing is not yet being applied in Turkey, it was presumed that these samples were unirradiated. The TL method requires that the inorganic components be separated from the sample. The reason for this requirement is that the polymineral phase emits radiation induced TL, whereas the organic phase produces non-specific signals. Therefore, TL intensity of whole samples depends on the degree of mineral contamination

The samples preperation, equipments and experimental procedure utilized in this work are described below.

3.2.1 Irradiation

About 250 gr each dried legume samples were placed into packed in polyethylene bags and sended to Nuclear Research and Training Center (ANAEM) Sarayköy-Ankara for irradiation. In order to simulate industrial food preservation processes, every aliquot of inorganic dust (that was used as TL dosimeter) was irradiated at room temperature at different doses by ^{60}Co gamma source at 1, 4, 8, 10 kGy with a dose rate of $\cong$1kGy/h in Nuclear Research and Training Center. After irradiation and until the date of the separation of minerals and analysis, the samples were stored in the cardboard containers.

3.2.2 Preparation of samples

Separation of the organic and inorganic phases is possible using different methods (plasma ashing, Soxhlet extraction, etc) but they are not very useful for daily routine. Therefore, a practical method of separation has been developed on the basis of the partial one described by chickpea and corn contains along with the organic phase an important amount of inorganic phase.

Firstly, each of the samples were grounded in hammer mill (Brook Cromphton, Wakfield, England). Seperation of the organic and inorganic phases was used as follow; about 50 g of grounded irradiated legume samples were immersed in 150 ml of carbon tetrachloride (CCI_4), and stirred for 3-4 h. $CC1_4$ was selected because it is an inert solvent; it does not damage the sample and has a good density for the aim (1.59 g/cm^3). Subsequent centrifugation showed clearly two different layers, the organic matter floating and the inorganic material at the bottom of the beaker. The two parts were separated by decantation and the mineral phase was washed several times using $CC1_4$. Since this phase still had some organic matter in it, the sample was treated with a mixture of hydrogen peroxide (H_2O_2) and sodium hypochlorite (NaCIO) (1:1) to remove as much organic matter as possible. In this method, no acid treatment was employed avoiding to eliminate carbonates.

Finally, the samples were dried and stored at room temperature in a desiccator with silica gel in the presence of sunlight to simulate similar conditions to that of production. This method of separation yielded about 4% of mineral material (20 g per 500 g from the whole samples of corn, and chickpea). When the inorganic phase was isolated, the samples were carefully crushed with a pestle) and mortar and sieved to obtain a size of the grain I under 50 urn. The powder was spread on stainless aluminium discs, about 5 mg on each one.

3.2.3 Data Analysis

The all glow curves were also analyzed by the Computerized Glow Curve Deconvolution (CGCD) method to obtain the number of glow peaks. This method has become very popular to obtain the number of glow peaks in the complex glow curves and their kinetic parameters for the last three decades [61]. It is apparent that if the number of data points used in the analysis increases, the potential for accurate evaluation of number of glow peaks and their kinetic parameters gets better. Therefore, this method has great advantages over the other methods.

However, it must be noted that different models, approximations and minimization procedures are used for the glow curve analysis in the CGCD program. As a consequence, one may wonder whether the results of CGCD method reflect the accurate kinetic parameters of the TL peaks. According to many experienced researchers, the results obtained by the CGCD method, in some cases, seem to be unreliable. Especially, the advantages of the CGCD method may be undermined in complex TL glow curves. As a result, many possible sets of kinetic parameters could be assigned to the same glow curve if different number of glow peaks was used in the CGCD program. Therefore, the number of glow peaks was only investigated by the CGCD method in the given study.

3.2.4 Measurement techniques

In order to simulate industrial food preservation processes, the reference samples were packed in polyethylene bags and were irradiated at room temperature at different doses, from 1 to 10 kGy, using a gamma source of ^{60}Co at a dose rate of 1 kGyh^{-1}. This irradiation was performed in the Irradiation Unit of ANAEM. After irradiation of all chickpea and corn, they were stored in the dark place at room temperature. TL measurement was carried out using a TL reader (Harshaw 3500, USA) with heat ranging from 30 to 400 ^{o}C at a rate of 1 ^{o}C/sec. The preparation of samples took place at room temperature.

The used CGCD program, which is based on the least square minimization procedure, was developed at the Reactor Institute at Delft, The Netherlands [62]. In this study, the first-order kinetics were approximated for all CGCD evaluations by the expression [63,64]:

$$I(T) = n_0 s \exp(-\frac{E}{kT}) \exp\left[-\frac{s}{\beta}\frac{kT^2}{E}\exp(-\frac{E}{KT}) * (0.992 - 1.620\frac{kT}{E}) \right] \tag{3-1}$$

where n_0 (m^{-3}) is the number of trapped electrons at t = 0, k (eVK^{-1}) is the Boltzman's constant. Other parameters were described in chapter 2. General-order kinetics were approximated by the expression,

$$I(T) = n_0 s \exp(-\frac{E}{kT}) \left[1 + \frac{(b-1)s}{\beta}\frac{kT^2}{E} \exp(-\frac{E}{kT}) * (0.992 - 1.620\frac{kT}{E}) \right]^{\frac{b}{1-b}} \tag{3-2}$$

The goodness of fit for all the measured glow curves was tested using the figure of merit (FOM) [65] as it is explained in chapter 2.3.4 with Eqn.(2.27). From many experiences, it can be said that, if the values of the FOM are between 0.0% and 2.5% the fit is good, between 2.5% and 3.5% is a fair fit, and >3.5% is a bad fit. Detailed information on the deconvolution method has been given elsewhere [61].

3.3 Results and Discussion

The general patterns of glow curves of irradiated and unirradiated leguminous are shown in Fig. 3.1 and 3.2. As seen, all glow curves have the similar shapes for irradiated samples. The similarities in TL glow curves observed between both samples seemed to be caused by the similarities in mineral composition after the separation of inorganic and organic phases. In these figures, comparisons of the TL glow curves from unirradiated leguminous (natural thermoluminescence glow curve, NTL) with glow curves obtained after irradiation gamma rays for different doses (induced thermoluminescence, ITL) are displayed. Glow curve was not found for unirradiated samples.

Generally, the TL intensities of minerals separated from irradiated samples were very much higher than those of unirradiated samples. The measurements performed on irradiated samples revealed that all of them (from 1 to 10 kGy) could be clearly discriminated from non-irradiated ones on the basis of the intensity of the TL signal. In fact, ITL glow curves of both samples exhibit the presence of a very intense peak at around 260 °C related to gamma-irradiation. The differences in the TL intensities from the unirradiated and irradiated samples are evident.

As seen in figure 3.1, the TL intensities of both samples increased with increasing irradiation doses. In the case of chickpea, the peak intensities increased from 9.45×10^5 a.u at 1 kGy to 5.13×10^6 a.u at 10 kGy. Similarly, in the case of corn, the peak intensities increased from 8.89×10^5 a.u at 1 kGy to 5.65×10^6 a.u at 10 kGy. Maximum TL temperatures of all irradiated samples are between the 250-280 °C temperature intervals.

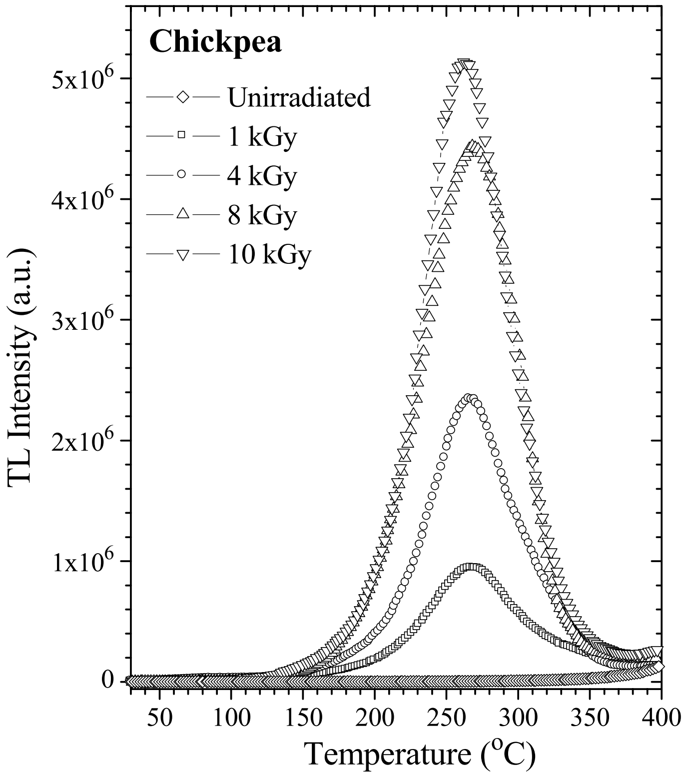

Figure 3.1: TL glow curves of irradiated chickpea at different doses (from 1 to 10 kGy) using a gamma source of ^{60}Co at a dose rate of 1 kGyh^{-1}. The measurements were made after 6 months of storage at RT of the irradiated samples.

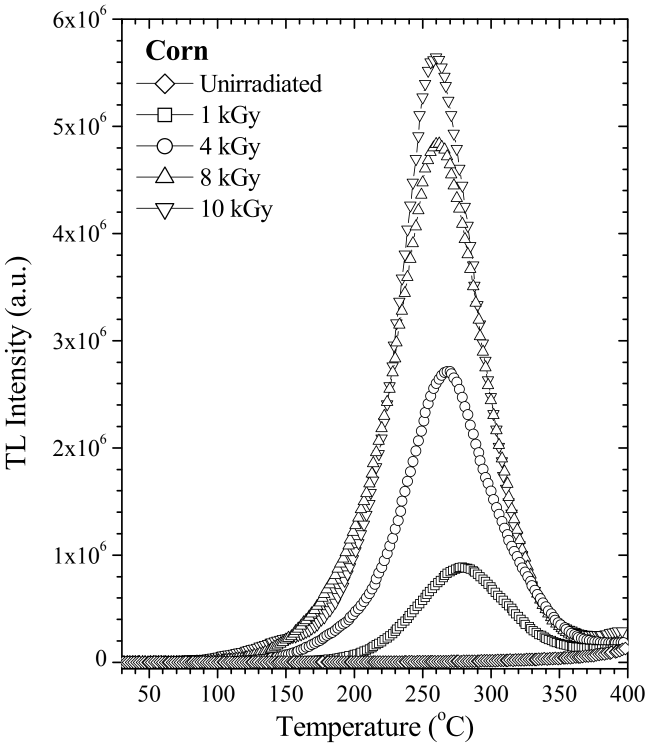

Figure 3.2: TL glow curves of irradiated corn at different doses (from 1 to 10 kGy) using a gamma source of ^{60}Co at a dose rate of 1 kGyh^{-1}. The measurements were made after 6 months of storage at RT of the irradiated samples.

All data in dose response are plotted on a log–log scale and shown in Fig.3.3. It is clearly seen that the obtained dose responses of glow peak by peak height method of both samples follow similar pattern and they are firstly increased linearly up to ≈8 kGy after it starts to saturate up to the end point of studied dose level (≈10 kGy). On the other hand, the calculated slopes of both curves are different from each other and the slope of the corn has greater than the chickpea.

The TL dosimetric characteristics of any material mainly depend on the sensitivity, energy response and the kinetic parameters quantitatively describing the trapping–emitting centers responsible for the TL emission. Thus, a reliable dosimetric study of a thermoluminescent material should be based on a good knowledge of its kinetic parameters. For example, the simultaneous estimation of the dose rate and the time elapsed since exposure are closely related to the position of the trapping levels within the band gap, and therefore it is necessary to have a good knowledge of these parameters.

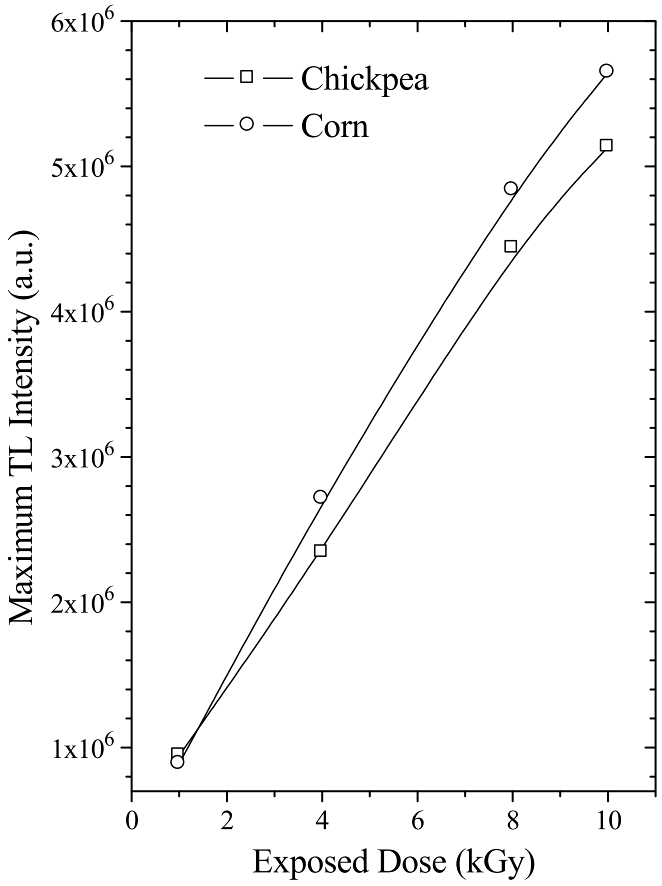

Figure 3.3: The TL dose response curves of glow curves of Chickpea and Corn samples determined by the peak height method.

There are various methods for evaluating the trapping parameters from TL glow curves [66]. When one of the glow peaks is highly isolated from the others, the experimental methods such as initial rise, various heating rates, and peak shape methods are suitable methods to determine them. However, in most materials, the glow curve consists of several overlapping peaks, which is also the case in the extracted minerals from the studied foods. When more than one glow peak is present in the glow curve, there are essentially two ways to obtain these parameters: the first is to isolate each individual TL peak from the others using partial thermal annealing treatment and the other is to make a complete glow curve analysis using deconvolution [67]. Therefore, the AD and PS methods along with the deconvolution method have been used to analyze the glow curves of studied samples [66-70].

As mentioned previously, the CGCD is another powerful technique in the study of TL. This technique is frequently used to analyze glow curves, it is also commonly used in the study dosimetric properties of TL dosimeters. The application of the CGCD technique for the decomposition of a composite TL glow curve into its individual glow peaks is widely applied since 1978 [71]. On the other hand, the previously published studies have shown that the determination of E_a and s mainly depends on the prior knowledge of b and the exact number of glow peaks which were used in the deconvolution program [72-73]. Therefore, to form an opinion about the b of all individual glow peaks in the glow curve structure of examined samples, the results of glow curves after different dose levels between 1 and 10 kGy were firstly utilized in the current study. This is a simple test for the first-order kinetics. In TL theory [74], the peak temperatures of glow peaks are expected to change only with heating rate for b=1. Hence, for a constant heating rate, the peak maximum should not be affected by other experimental parameters and should be fairly constant within the limit of experimental uncertainties. However, for $b \neq 1$ and below the trap saturation points {n_o(concentration of trapped electrons)<N_t (concentration of traps)}, it is generally received that the peak temperatures are shifted to the lower temperature side with increasing dose levels.

It is seen from Figs.3.1 and 3.2 that the structures of the TL glow curves of both samples and the peak temperatures of glow curves were slightly changed with increasing dose levels. These results indicate that the measured all glow curves for different doses might be considered under the general-order kinetics. As a result, after many tries with different number of glow peaks, it was concluded that the glow curves of corn under different doses are well described by a linear combination of at least two closely overlapped glow peaks corresponding to temperatures at around 195 ^{o}C and 260 ^{o}C, respectively. Therefore, the glow curves of corn were always fitted with two components. These peaks are probably due to the combined TL of quartz and feldspar minerals. An analyzed glow curve of corn measured after 8 kGy irradiation at RT is shown in figure 3.4 along with the components obtained from CGCD. The obtained kinetic parameters were given in Table 3.1. The statistical error of these parameters deriving from the analysis of glow peaks after different irradiation doses is of the order of 10%. On the other hand, it was observed that the glow curves of chickpea under different dose levels are always well fitted by one general-order glow peak (see Fig.3.5). The FOM values for both of the corn and chickpea were found 1.11. This results can be said that the fit is good. The obtained kinetic parameters of this peak were also given in Table 3.1.

Table 3.1: The trapping parameters of chickpea and corn samples calculated by the CGCD method (Heating Rate= 1 ^{o}C/s).

Trapping Parameters	Chickpea	Corn	
	Peak 1	Peak 1	Peak 2
T_m (^{o}C)	270	195	262
E_a (eV)	0.804	0712	1.048
ln(s) (s^{-1})	13.72	14.38	19.51
b	1.22	1.01	1.87

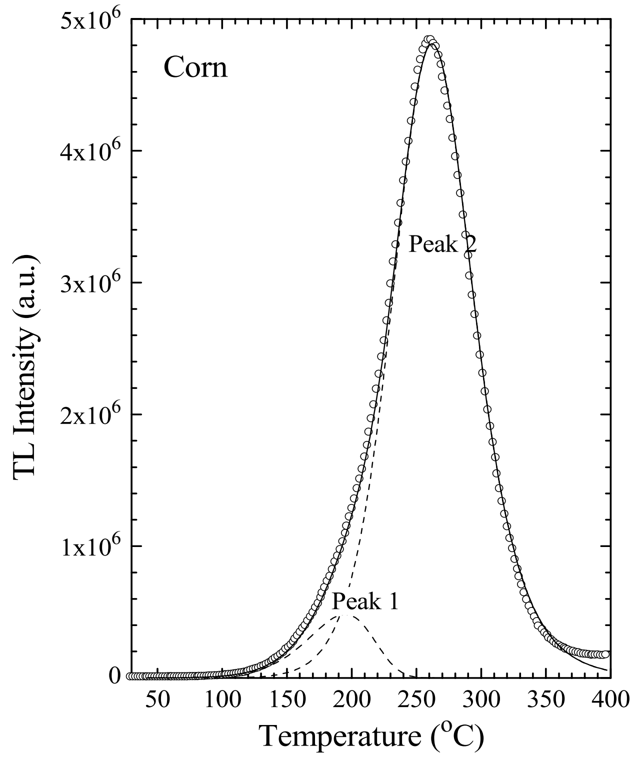

Figure 3.4: An analyzed glow curve of corn measured after 8 kGy irradiation at RT. The glow curve was measured immediately after irradiation of the sample at a heating rate of 1°C s^{-1}.

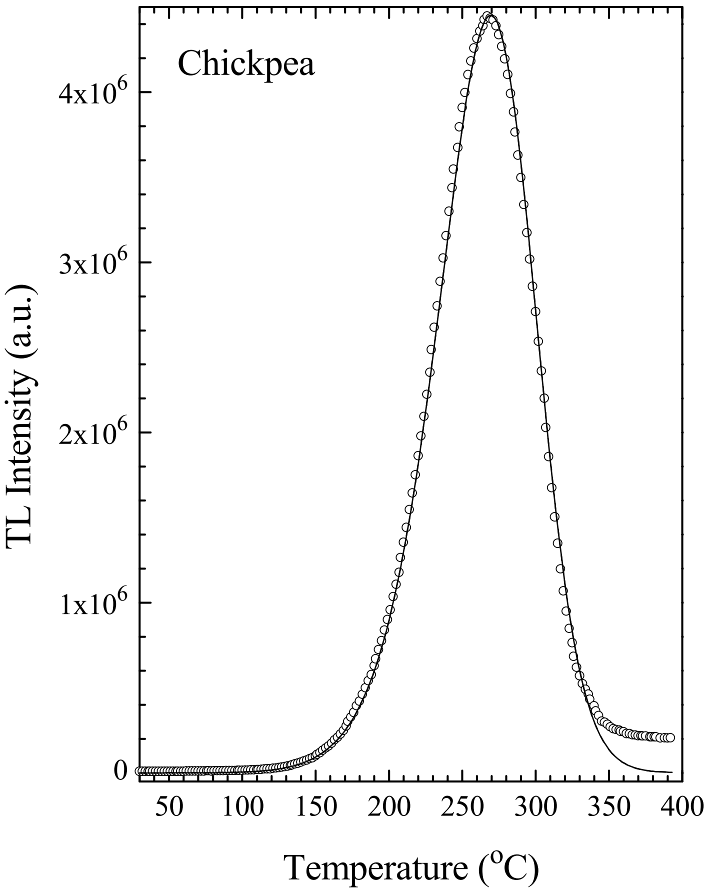

Figure 3.5: An analyzed glow curve of chickpea measured after 8 kGy irradiation at RT. The glow curve was measured immediately after irradiation of the sample at a heating rate of 1°C s^{-1}.

The stability of the stored signal at normal temperatures is an important factor in many applications such as archaeological and geological dating, personal and environmental dosimetry. Any appreciable decay in the stored signal at room temperature will invalidate the relationship between TL emitted and the radiation exposure that may have been delivered some considerable time before readout. The extent of TL signal decay over long periods is difficult if not impossible to measure directly, particularly in archeological applications.

Therefore, some studies were done in order to check the evolution of the TL signals with the elapsed time since the irradiation process took place; i.e. an attempt to establish the stability of the TL signal of irradiated samples over time. In this sense, some measurements were made after increasing storage periods of time, until 6 months for doses to be exact 4 kGy. The normalized relative responses of analyzed glow curves of both samples at the end of the planned storage periods by CGCD method are shown in Fig.3.6. Each point in the figure is the average of at least two readings. The behavior of every curve, regardless of the dose absorbed by the sample, is similar in all the cases. The TL yields of glow peaks of chickpea and corn samples were reduced to typically ≈50% and ≈55% of their original values after six month storage at RT, respectively.

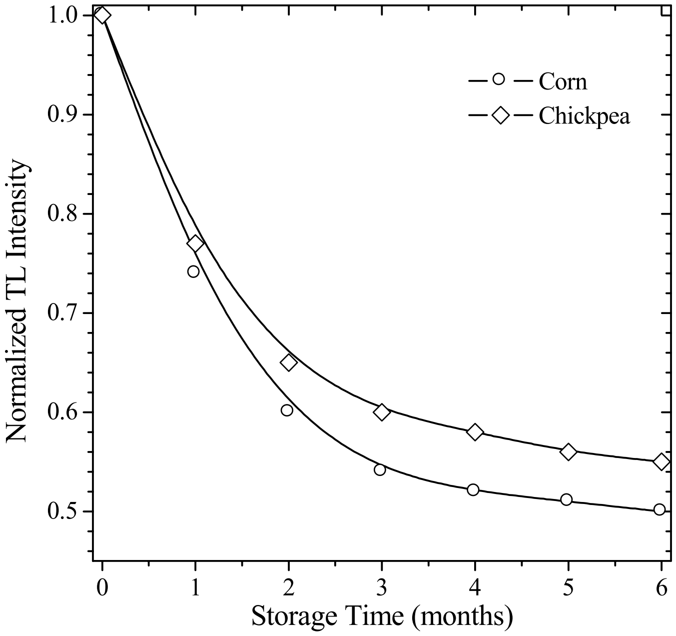

Figure 3.6: The obtained fading characteristics of glow peaks of corn and chickpea using the CGCD program.

3.4. Conclusions

In this study focuses on (i) the confirmation of the validity of TL as a method to discriminate between irradiated and non-irradiated irradiated chickpea and corn; (ii) the characterization of the TL glow peaks;(iii) the determination of the dependence of TL intensity with different doses; and (iv) the modeling, from irradiated samples, of the stability of TL signal with time.

This study was carried out to establish a detection method for irradiated legumes (chickpea and corn) through thermoluminescence (TL). The legumes were packed in polyethylene bags and were irradiated using a ^{60}Co source with dose of 1, 4, 8 and 10 kGy, respectively. TL intensities of the minerals were measured by TL. It was observed that the extracted samples from both legumes exhibit good TL Intensity and the TL intensity of glow curves of them increased proportionally to irradiation doses.

Maximum TL temperatures of both irradiated legumes were below 400 ^{o}C, within the 150-350 ^{o}C temperature interval recommended for evaluation. A glow curve was not found for unirradiated samples. The TL kinetic (trapping) parameters of overlapping peaks were estimated by computerized glow curve deconvolution (CGCD) method. Fading observations of TL after irradiation at 4 kGy, show the same behavior in all the cases: an initial rapid decay to maintain a certain stability from 3-4 months onwards.

Generally, the TL intensities of minerals separated from irradiated samples were very much higher than those of unirradiated samples. The measurements performed on irradiated samples revealed that all of them (from 1 to 10 kGy) could be clearly discriminated from non-irradiated ones on the basis of the intensity of the TL signal. In fact, ITL glow curves of both samples exhibit the presence of a very intense peak at around 260 ^{o}C related to gamma-irradiation.

The differences in the TL intensities from the unirradiated and irradiated samples are evident. As seen, the TL intensities of both samples increased with increasing irradiation doses. In case of chickpea, the peak intensities increased from

$9.45x10^5$ a.u at 1 kGy to $5.13x10^6$ a.u at 10 kGy. Similarly, In case of corn, the peak intensities increased from $8.89x10^5$ a.u at 1 kGy to $5.65x10^6$ a.u at 10 kGy. Maximum TL temperatures of all irradiated samples are between the 250-280 ^oC temperature intervals, whereas unirradiated samples did not exhibit glow peak. The FOM values for both of the corn and chickpea were found 1.11. This results can be said that the fit is good.

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