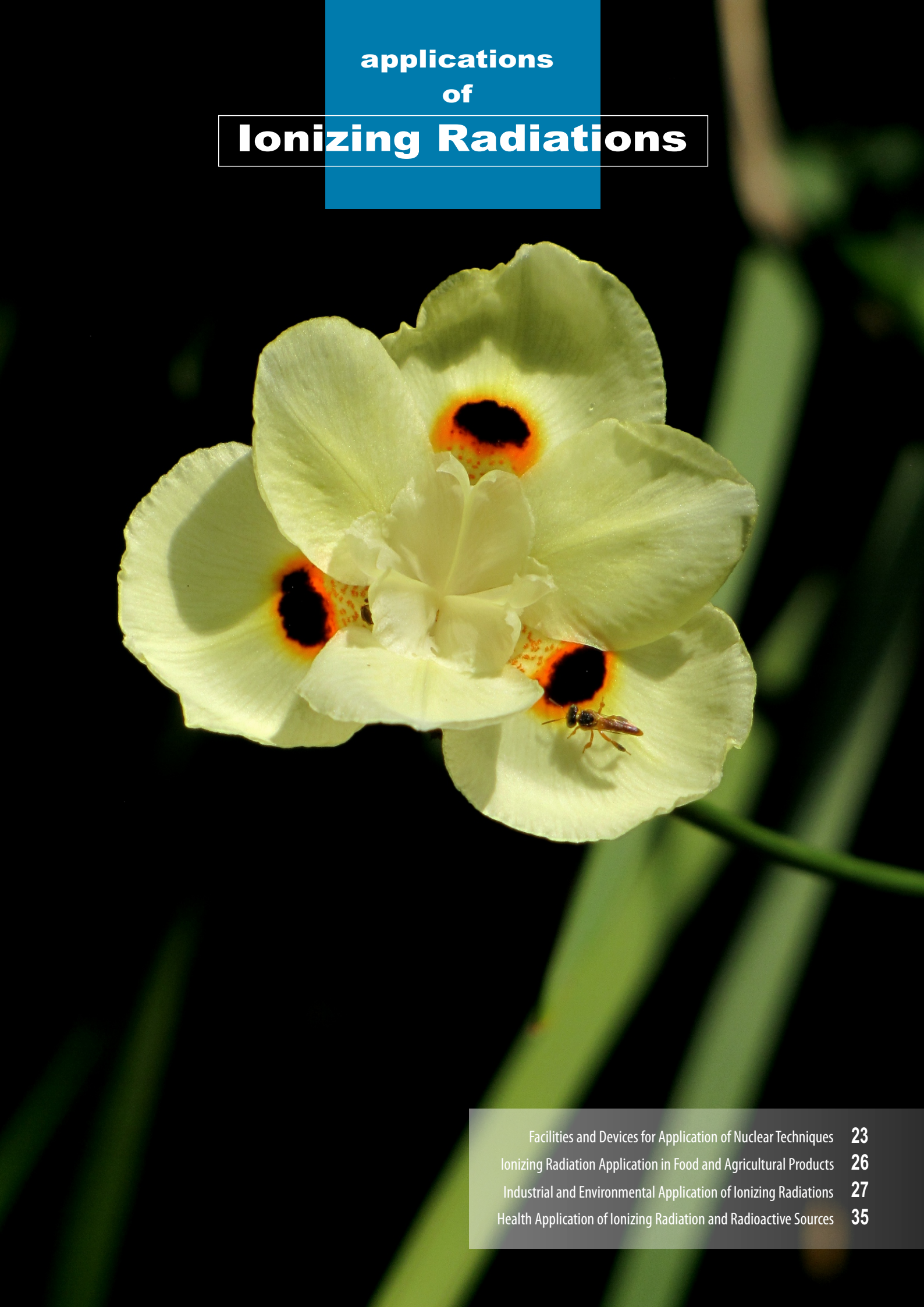
# applications of Ionizing Radiations



# introduction

The dynamism to be always developing new technologies, associated with the advancements of other fields, is the main characteristic of the nuclear technology application. The environmental preservation, radio-sterilization, grafting, curing, nanotechnology and polymer production are strongly associated with radiation processing and have being consolidated with the development of new irradiators. The progress of the instrumentation and information technology has stimulated the development of innovative gamma industrial tomography system for the optimization of multiphase industrial process. Basic research and nuclear technology application in the fields of food science, biomaterial, and nanotechnology have been improved continuously. Others fields, such as dosimetry, nuclear instrumentation and industrial electron beam, X-ray and gamma ray irradiators have been accomplished, showing their importance in the innovation of nuclear technology applications. As long as the processes, considered innovative in the present days, prove to be environmentally safe and economically more interesting, new nuclear applications tend to be standard in many areas. To follow this trend and to keep update, the Radiation Technology Center (CTR) Brazil has been working to spread the nuclear application techniques with new developments in standard applications and brand new nuclear technologies, with high impact on the future of the agriculture, medicine, industry and the environmental preservation. The CTR mission is “to apply the radiation and radioisotope technologies in Industry, Health, Agriculture, and Environmental Protection, expanding the scientific knowledge, improving human power resources, transferring technology, generating products and offering services for the Brazilian society”.

The CTR main R&D activities are in consonance with the IPEN Director Plan (2011-2013) and the **Applications of Ionizing Radiation Program**, with four subprograms:

- Irradiation of Food and Agricultural Products;
- Radiation and Radioisotopes Applications in Industry and Environment;
- Radioactive Sources and Radiation Applications in Human Health; and
- Radioactive Facilities and Equipment for the Applications of Nuclear Techniques.

Nowadays, the CTR has three gamma ray ($^{60}$Co) irradiators: Gammacell, Panoramic and industrial-scale multipurpose types, and two industrial electron beam accelerators of 1,5MeV. These installations give support to the local scientific and industrial communities on the development of processes and products, filling up the gaps on the field of the application of radiation processing in the modern economy of the XXI century, particularly in: food processing, heritage preservation, biomass pretreatment, environmental protection and health protection, as well as in the development of advanced materials together with researchers and engineers from research Institutes and companies. Also, primarily EBA applications, such as treatment of wire, electric cable, heat-shrinkable tubing and film and tires, as well as $^{60}$Co Irradiator application for sterilization of healthcare products that require rapid turnaround are routinely carried out using both installation types. The improvement of the activities of radioisotope and radiotracer technology applications in the petrochemical and chemical industries, for processing control and sanitation, and studies on the fields of nanotechnology and nanocomposites may also be emphasized.

It should be highlighted that the success and achievements reached are credited to the financial support to our national projects by the funding organizations FAPESP, CNPq, CAPES and FINEP, and to international projects, such as Technical Cooperation (TC) and Research Contract (RC), supported by the IAEA, as well as the national and international partnership and cooperation with industries, universities and institutions.

The Radiation Technology Center (CTR) has two Industrial Electron Beam Accelerators of 97.5 kW (1.5 MeV - 65 mA) and 37.5 kW (1.5 MeV - 25 mA), supplied by IBA Industrial Inc. and two small-scale cobalt-60 Irradiators: Gammacell (2,142 Ci Dec - 2010) and Panoramic (394 Ci Dec-2010).

Further facilities include a semi-industrial Multipurpose Gamma Irradiator, category IV (IAEA -SSG8) developed with Brazilian technology (76 $m^2$). This irradiator can be operated in stationary and continuous modes (product overlap sources) and the source design capacity of cobalt-60 is 37 PBq (1 MCi). The installed activity of this facility is 4,5 PBq (122 kCi - Jan 2014) with 32 cobalt-60 pencils. The coming months will be installed 7,4 PBq (200 kCi) of cobalt-60 increasing the total installed activity to 12 PBq (322 kCi) approximately. The poly-methylmetacrylate (PMMA) dosimetry system provided by Harwell Dosimeters Ltd. - UK, certified by the International Dose Assurance Service (IDAS) of the International Atomic Energy Agency (IAEA) is used to control the absorbed doses in the products. Currently, the facility is beginning to apply the alanine pellets (Radspin) dosimetry system to increase the functional dose range.

The Electron Beam Accelerator, the small-scale cobalt-60 irradiators and the Multipurpose Gamma Irradiation Facility have been providing services on radiation processing, mainly for sterilization of health care and disposable medical products as well as support to research studies on modification of physical, chemical and biological properties of several materials. Almost all disposable supplies used by the Radiopharmacy Center - IPEN to produce technetium-99m generators and other medical radioisotopes are continuously sterilized by the Multipurpose Gamma Irradiation Facility. Many biomedical research laboratories and center especially those working with equipment for cell cultures and vaccine production also make use of the gamma sterilization. Animal feed and shavings used by certified bioteries are routinely disinfected. Alternative underwater irradiation methods were developed to meet the demand of gemstone color enhancement using gamma radiation. Human tissues including bone, skin, amniotic membranes, tendons, and cartilage belonging to National Banks tissues are routinely irradiated. In particular, disinfestations and disinfection processes applied on cultural heritage objects (books, wood, paintings, furniture, etc.) using gamma radiation were intensified the last three years. Additional activities developed by these facilities include: preservation and disinfestations of food and agricultural products; treatment of industrial and domestic effluents, sludge and hospital waste; paints, varnishes, adhesives and coating cure; polymer grafting and modification; radiation processing of composite materials and natural polymers. In 2013, more than 1000 $m^3$ of medical, pharmaceutical, and biological products were radiosterilized by the Multipurpose Gamma Irradiation Facility.

Annually, 3,530 km of wire and electric cables for chemical, automobile, aircraft and electro-electronic companies have been irradiated in the Industrial Electron Beam Accelerator. The radiation processing promotes crosslinking among the polymeric chains, increasing electrical, thermal, mechanical, and chemical properties. The modernization of the installation promotes the elevation of wire and electric cables processing velocity to 300 m/min and polyethylene foams to 15 m/min, becoming the product prices more competitive in the Brazilian market.

### Industrial dosimetry in radiation processing

In radiation processing, a well characterized reliable dosimetry system that is traceable for recognized national and international dosimetry standards is the key element of such activities. The Industrial Dosimetry Laboratory/CTR has the responsibility to measure the radiation dose absorbed in the processes induced by ionizing radiation at Co-60 gamma ray irradiation (Gammacell, Panoramic and Multipurpose Irradiator) and electron beam (two Industrial Electron Beam Accelerators of 97.5 kW and 37.5 kW) facilities in ordinary services and to develop new products and services by radiation processing. The dosimetry procedures for radiation processing are carried out in agreement with the ISO (International Organization for Standardization) - ASTM (American Society Testing and Materials) standard guides and practices. To establish a reliable dosimetry system, the laboratory has participated of the intercomparisons of gamma dose measures, organized by International Dose Assurance Service (IDAS) offered by the International Agency Energy Atomic (IAEA) and of the national intercomparisons to check on the entire radiation dose measurement system: dosimeters, measurements equipment, and irradiation and data procedures. The dosimetry systems used for the quality control of the radiation process are: Fricke solution as reference standard dosimetry system, Alanina as transfer standard dosimetry system and as routine dosimetry.

### Formation of ozone gas in industrial irradiation system

In industrial irradiators facilities there are a layer of air between the source and product. The radiation interacts with this air layer, causing radiolysis effects on the molecules present, and the main interaction are with the oxygen molecules that have their bonds broken, separating them into two highly reactive atoms that recombine with the other molecule of oxygen to form ozone gas. In the troposphere, ozone acts as a protective layer, shielding the earth's surface from ultraviolet rays of high energy from the sun. Because it is highly reactive, ozone at the earth's surface is harmful to plants, animals, and humans. Chronic exposure to ozone can cause morphological, immunological, biochemical and functional lung and contribute to tumor formation. In facilities with gamma radiation, X-rays, or electron accelerators, the ozone produced interacts with the surface of treated products and structural elements of the radiators, and the high concentration of this harmful gas is an issue of job security inside its chambers irradiation, especially when access is required for operators to perform maintenance work. The formation, decay, and dispersion of ozone in industrial gamma irradiators facilities that use cobalt-60 was studies through the monitoring of ozone concentration by optical absorption method in a commercial monitor.

### Radiation detectors and tomographer

**Purification and growth of $HgI_2$ crystals from physical vapor transport for application as radiation detectors**

A great interest has been focusing on the development of a room temperature radiation detector, using semiconductor materials that have high atomic number and wide band gap. This type of detector has a large applicability as X-ray and gamma ray spectrometer, operating at room temperature. Layered semiconductor materials have a number of properties that make them attractive for such application. However, the role of crystal impurities on the detector performance is crucial, then improvements on the chemical purification and the impurity reduction analysis should be achieved. The physical vapor transport (PVT) technique was established for the purification and growth of $HgI_2$. For purified crystals a deep red color and glossy surface (Fig. 1A) were observed, while the crystal grown once presented a non uniformity dark red color, being more accentuated in the upper region (Fig. 1B).

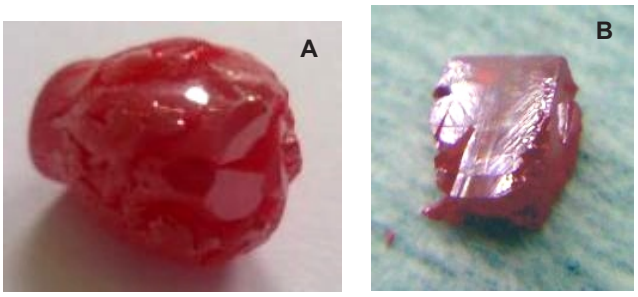



Figure 1. Iodide mercury crystals growth at IPEN.

There was a significant reduction of the impurities after each purification, indicating the effectiveness of the purification by the PVT technique. Also, a structure with uniform layers (Fig. 2C) may be observed, indicating good orientation in the purer crystal structure. The image of the residual salt surface layer, after the growth, showed an amorphous structure (Fig. 2D), as expected.

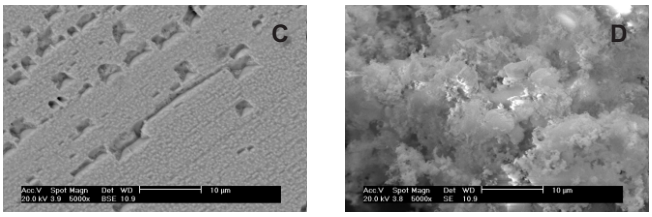



Figure 2. Micrographs of the $HgI_2$: crystal surface grown by PVT (C) and residual salt after the crystal growth (D).

A significant improvement in the $HgI_2$ radiation detector performance was achieved for purer crystals, growing the crystal twice by the PVT technique.

**Semiconductor radiation detectors to be operated at room temperature**

Silicon PIN photodiodes (SFH 00206 type) has been used as routine dosimeters for irradiation processes performed with a Cobalt-60 Panoramic Irradiator facility in the dose-rate range of 8.1 Gy/h-125 Gy/h. For doses up to 15 kGy, it was not observed any radiation damage what confirms the reproducibility of the diode response better than 3%. Due to the good spatial resolution of the diode it was possible to measure the transit dose due to the movement of the Cobalt-60 radioactive source as well the dose-rate mapping in the Panoramic Irradiator.


Figure 3. Low-cost pin diode dosimeter probe.

**MCZ diode response as a high-dose gamma radiation dosimeter**

Epitaxial and FZ tolerant radiation silicon diodes processed at the University of Hamburg and Helsinki Institute of Physics have been successfully used as on-line dosimeters for:

a) diagnostic radiology, mammography and computed tomography, in the 28 kV to 150 kV range at a total dose of 200 kGy;
b) in radiation processing with total doses up to 5 MGy and
c) as clinical electron and gamma beams.

In this range, the dosimetric response of the diodes is linear. This work was partially supported by CNPq via contract 480167/2011-7

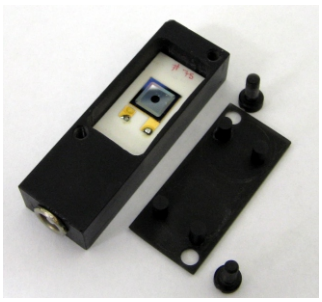
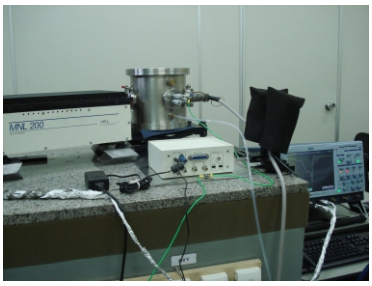


Figure 4. Epitaxial radiation-hard Si diode probe.

**Measurements of electron transport parameters in avalanche regime**

The goal of this work is to measure the most important electron transport parameters in gases (first Townsend coefficient and the electron drift velocity) for simulation and modeling of radiation detectors and plasma discharges at high uniform electric fields. The method applied was the Pulsed Townsend technique, where the primary ionization is produced through the incidence of a nitrogen laser beam onto a metallic electrode (cathode). The heart of the chamber is an RPC like cell with a bulk aluminum anode and a glass cathode. The signal is readout with a fast digitizing oscilloscope to record the fast signal induced by the electron movement in the thin gas gap. A set of data with nitrogen, isobutene, and butane was collected in collaboration with the Laboratory of Instrumentation and Experimental Particle Physics - Coimbra, Portugal. This work was co-financed by FAPESP under Contract 02/04697-1, by CNPq via contracts 478859/2009-0 and 479079/2010-2 and partially supported by Fundação para a Ciência e a Tecnologia, Portugal (contract CERN/FP/116392/2010).

Figure 5. RPC like cell with a bulk aluminium anode and a glass cathode and experimental apparatus.



**Development of the inorganic scintillator crystals used as radiation detector**

The laboratory of scintillator crystal growth develops pure and doped crystals for the construction of radiation detectors. Inorganic scintillators play an important role in the detection and spectroscopy of gamma and X-rays, as well as in neutrons and charged particles. For a variety of applications, new inorganic scintillation materials are being studied. New scintillation detector applications arise continuously and the interest in the introduction of new fast scintillators becomes relevant. Scintillation crystals based on cesium iodide (CsI) have relatively low hygroscope, easy handling, and low cost, features that favor their use as radiation detectors.

Pure and doped CsI crystals are grown using the Bridgman technique. In this technique, the charge is maintained at high temperature for 10 h for the material melting and complete reaction, using a quartz crucible in vacuum atmosphere. The temperature gradient 21°C/cm and 1 mm/h descending velocity were chosen as technique parameters. After finishing the growth, the furnace is cooled at a rate of 20°C/h to room temperature. The best doping element concentration is studied. The main used dopants are thallium (Tl), bromine (Br), lead (Pb) and Lithium (Li). The grown crystals are subjected to heat treatment. In this procedure it is used vacuum of 10-6 mbar and continuous temperature of 350ºC, for 24 hours. In the figure 6 CsI crystals doped with bromine are shown.

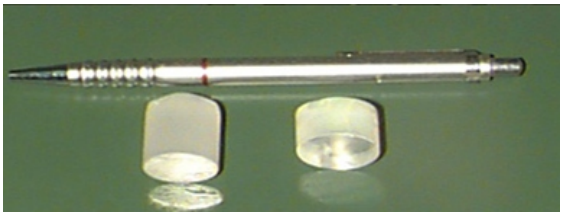


Figure 6. CsI:Br crystals with concentration $10^{-2}$ M.

For the detection system crystals are coupled optically to the photocathode. The bright photons move the electrons of photocathode and these are accelerated by a series of electrodes (dynodes) inside the photomultiplier tube. In the scintillation detection process, the proportionality is maintained in each step, that is, the number of photons released by the crystal is proportional to the energy released in crystal, from the incident radiation. The number of displaced electrons in the photocathode is proportional to the number of light photons from the crystal and the electric current generated by the photomultiplier tube. This way the height of the electrical pulse from the photomultiplier tube is proportional to the radiation energy absorbed by the crystal. This allows that the energy from different radionuclide can be distinguished from each other by pulse height. Measurements of pulse height using gamma radiation sources of $^{54}$Mn (835 keV) and $^{137}$Cs (662 keV) are show in Figure 7 and Figure 8.

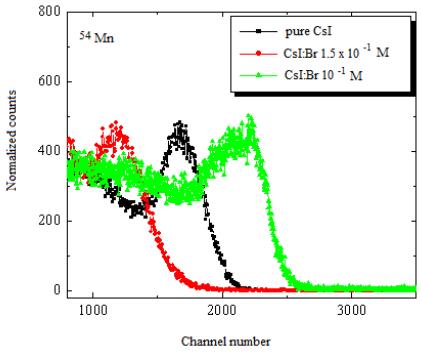



Figure 7. Pulse height obtained for gamma radiation from $^{54}$Mn (835 keV) source with crystals of CsI:Br and pure CsI.

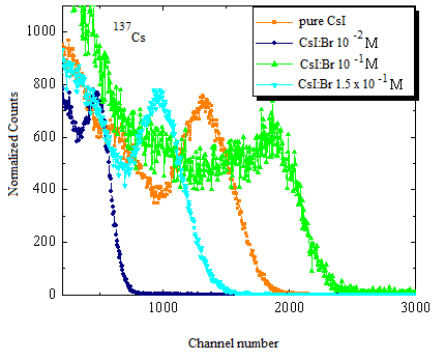



Figure 8. Pulse height obtained for gamma radiation from $^{137}$Cs (662 keV) source with crystals CsI:Br and pure CsI.

**Development of an industrial tomography using three different gamma ray energies simultaneously**

Usually, the analyzed objects in the industrial tomography field, such as distillation columns and engines, contain materials with a large range of densities, for example iron (7.8 g/cm$^3$), aluminum (2.7 g/cm$^3$), water (1.0 g/cm$^3$), gases (0.000125 g/cm$^3$). Thus, ideally, radioactive sources containing different gamma energies should be used. The combination of $^{137}$Cs with $^{192}$Ir or $^{137}$Cs with $^{75}$Se could be used as their energy spectra present energy peaks of 662, 468, and 317 keV for a $^{137}$Cs + $^{192}$Ir combination or 662, ≅132 keV, ≅269 keV and 401 keV for a $^{137}$Cs + $^{75}$Se combination. Moreover, in case the object to be analyzed contains high-density material, the $^{60}$Co (1173 and 1332 keV) can be included in the source combination to allow the beam to cross the materials. However, depending on the density and dimension of the object the $^{241}$Am (59 keV) can be added to the source combination in order to improve the image quality in the regions where low density material is present. A third generation multi-source transmission computed tomography system with a multichannel data acquisition electronic system (Fig. 9) was developed at IPEN. In its configuration, an array of five NaI(Tl) detectors of 5x5 cm (diameter, thickness) were placed on a gantry, in an arc, opposite the gamma ray sources. The entire apparatus (gantry with detectors and gamma sources) rotated around the stationary object, by means of a stepper motor controlled by a host computer. The five NaI(Tl) detectors were individually collimated with lead. Two different radioactive sources, $^{192}$Ir (≈317 keV yield = 87%; 468 keV yield = 48% and 604 keV yield = 8%) and $^{137}$Cs (662 keV) were placed in a single lead collimation system.

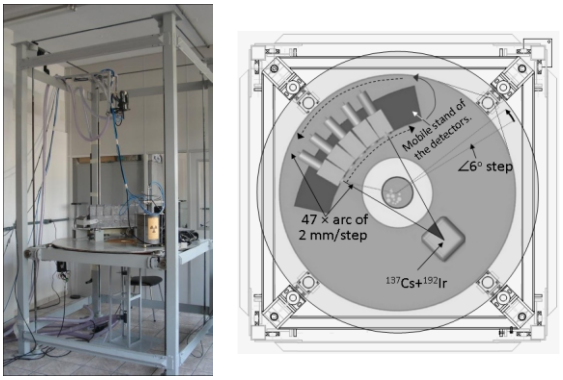



Figure 9. The third generation multi-source transmission computed tomography developed at IPEN.

**Tomographic measurement in the bubble column**

The capacity of the developed IPEN multisource tomography (CT) to analyze bubble column for industrial processes, determining and differentiating the attenuation coefficients of materials with different phases (gas, liquid and solid) was studied using a bubble column (ϕint=8 cm). gas absorption column. The multisource CT system was capable of determining as well as differentiating the attenuation coefficients of materials with two phases (gas and liquid). It was also able to provide important information concerning the hydrodynamics occurring inside a multiphase column. The Fig. 10 illustrates three possibilities to understand multiphase phenomena that occur in the experimental bubble column. Despite the first (Fig. 10 (A)) is easier to obtain, in practice it is almost impossible in an industrial environment because columns are generally opaque and its interior is rough and inaccessible. The other two possibilities are non-invasive contributions of the tomography technology. The holdup of water and air for each position of the column (ϕint=8 cm) are shown in Fig. 10.

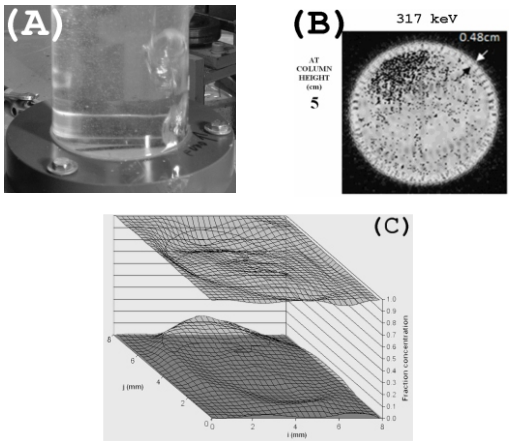



Figure 10. For each (i,j)-th pixel from the reconstruction image (B) the cW and cA were calculated solving a matrix system. Concentration gradients of water and air (C) in column at five cm above bubble generation (A). The arrow indicates bubble generation placed at 1.5 cm from the column wall in bottom of column.

Several works have been performed to evaluate the effects of ionizing radiation on different kinds of food, such as: meat, through lipid peroxidation analysis in salmon and beef burgers; grains, physical, microbiological and sensorial tests in soybean, peanuts, pistachio; herbs, microbiological and sensorial analysis of medicinal herbs; vegetables, effects of gamma radiation on ready-to-eat vegetables. Besides food analysis, other studies evaluated the decontamination of biological ferment by gamma radiation and the radiation degradation of biological residues (aflatoxins) produced in food laboratories. Actually the main research field of includes the analysis and detection of irradiated foods with focus on chemical interaction of bioactive molecules, food safety, consumer acceptance and sensory aspects, phytosanitary and quarantine measures studies, detection of irradiated foods.

A main project has been carried out and covers “Application of ionizing radiation in foods for people with specific diets”. This project is Coordinated Research Project from International Atomic Energy Agency (IAEA 16226). Contacts with hospitals continue in slow motion. People responsible for these areas showed strong reluctance in accept the idea and to contribute with any effort in this direction. It was made contacts with several nutritionists totalizing six hospitals, besides isolated initiatives. One hospital is public and five are privates, all of them are main hospitals in São Paulo. One is the most important clinical hospital in Latin America and the others, in somehow, have a peculiar characteristic, being a reference hospital in a specific field. We have the willingness to continue with the sensory plans for nutritionists but it seems increasingly remote at this moment. The main reasons are extensive bureaucracy of internal departments of hospitals and certain apprehension by staff to take the matter further. Meanwhile a questionnaire was delivered for them in order to survey the situation about food served and prescribed to immune-compromised patients. The questionnaire was based on Hungary initiative (showed in last RCM meeting) and it had 20 questions. Until now we received a feed back of two hospitals.

A special invitation from Brazilian Institute of Cancer Control - IBCC resulted in a 45 min. presentation to around 120 attendees consisting mainly of radiologists and students of radiology. The presentation covered an introduction on food irradiation subject and a second part covering this project. A degustation of irradiated food (baby carrots, pineapple, and ice cream) was carried out. The results were very favorable: for pineapples, 61% liked very much and 34% liked moderately (average score of 6.6 in 7); for baby carrots, 46% liked very much, 46% liked, 4% neutral and 4% disliked very much (average score of 4.2 in 5); for ice creams, 37.7% liked very much, 49.2% liked, 6.6% neutral, 4.9% disliked and 1.6% disliked very much (average score of 4.2 in 5); Two questionnaires were delivered in the occasion.

Figure 11. Degustation of irradiated food.

## Modification and preparation of polymeric materials and composites

**Application of pigment black charcoal in low density polyethylene and influence of the ionizing radiation**

This work studied the development of charcoal black pigment which has similar characteristics of those already used in the market of thermoplastics processing. Nowadays, the often used is the carbon black which generates many toxic residues that when released into the atmosphere increases air pollution. The aims of this research were to study the obtainment of charcoal black pigment; the performance of this pigment by comparing it with the carbon black; the incorporating of the pigment obtained in low density polyethylene (LDPE) and the characterization of the product and the influence of the ionizing radiation on it. The black pigment obtained was incorporated into LDPE and characterized in relation at their stability during injection, dispersion, migration, and color coverage. Mechanical tests were also performed with non irradiated and irradiated samples at irradiation doses of 100, 200, 300 and 400 kGy. The incorporation of the pigment into the polymeric matrix during the injection process was easy. The obtainment charcoal black pigment is less harmful to the environment, since it is not a petroleum product as carbon black but by incomplete combustion of wood. This is obtained from renewable sources. Thus it will be produced charcoal for the production of the pigment to be inserted in the industrial chain. Despite using 1.4% of this pigment, it is easy to obtain it from a renewable source, and low cost besides presenting colorimetric properties compatible with the carbon black. Regarding the irradiated samples can be said that there was an increase in the majority of properties studied. Depending on the intended use of the polymer can irradiate it in the most appropriate dose which had improvement in their properties.

**Use of ionizing radiation in the recycling of unserviceable tires of automotive and ITS adequate environmental disposal**

The aim of this study was to use ionizing radiation in the recycling of scrap tires of automotive. Samples of rubber unserviceable tires were irradiated with radiation doses 200, 400, and 600kGy in an electron accelerator. Subsequently, they were characterized by thermogravimetry (TG), differential scanning calorimetric (DSC), and tensile strength mechanical test, spectrophotometer Fourier transform infrared (FTIR) and scanning electron microscopy (SEM). By thermogravimetry was possible to observe the effects of radiation in the mass loss of material. In the DSC curves were observed exothermic decomposition peaks and associated values of enthalpy variation (ΔH). The mechanical properties of the elastomeric matrix with unserviceable tires powder were studied and its behavior to ionizing radiation was analyzed. FTIR spectra were obtained in the 4000 - 650 $cm^{-1}$ region. It was observed that there was no change in the peaks due irradiation. For SEM the micrographs were enlarged from 32 times up to 1000 times and observed in sizes from 1mm up to 20 µm. It was observed at doses of 200 and 400 kGy, roughness corresponding to breaks or ruptures possibly caused by radiation. In 600 kGy radiation dose was observed cavities caused by radiation. It was observed that at all doses occurred degradation. For samples without powder and with 10, 30 and 50% of unserviceable tires powder it was obtained micrographs of 100 µm and 200 µm amplification. Also it was possible to observe the incorporation of unserviceable tires powder of automotive in the elastomeric matrix of non-irradiated and irradiated samples. Thus it was possible give an environmental disposal for this residue.

**Application of gamma radiation in the determination of physical parameters in woods**

Due to availability and particular features, wood was one of the first materials used by mankind with a wide variety of applications. It can be used as raw material for paper and cellulose manufacturing; in industries such as chemical, naval, furniture, sports goods, toys, and musical instrument; in building construction and in the distribution of electric energy. Wood has been widely researched; therefore, wood researchers know that several aspects such as temperature, latitude, longitude, altitude, sunlight, soil, and rainfall index interfere with the growth of trees. This behavior explains why average physical-chemical properties are important when wood is studied. The majority of researchers consider density to be the most important wood property because of its straight relationship with the physical and mechanical properties. There are three types of wood density: basic, apparent and green. The apparent density was used here at 12% of moisture content and green density for living trees. In this study were used woods of various densities of seven different species of trees, namely: “freijó”, “peroba mica”, “jequitibá”, “muiracatiara”, “cumaru”, “sucupira” and “ipê”. For wood density determination by non-conventional method, $^{241}Am$, $^{133}Ba$, $^{192}Ir$, $^{60}Co$ and $^{137}Cs$ gamma-ray sources, a NaI scintillation detector and a counter were used. The results demonstrated this technique to be quick and accurate. By considering the nuclear parameters obtained as half value layers and linear absorption coefficients, $^{137}Cs$ demonstrated to be the best option to be used for inspection of the physical integrity of electric wooden poles and living trees in the laboratory simulation.

**Investigation of the effect of ionizing radiation on composites based on biodegradable polymers and coconut fiber**

The market for biodegradable polymers had shown strong growth from 2001 up to 2005. A number of major plant expansions for commercial scale production had been planned. The major classes of biopolymers, polylactic acid and aliphatic-aromatic co-polyesters has been used in a wide variety of niche applications, particularly for manufacture of rigid and flexible packaging, bags and sacks and foodservice products. In 2005, starch-based materials were the largest class of biodegradable polymer and polylactic acid (PLA) was the second largest material class followed by synthetic aliphatic-aromatic co-polyesters. Product development and improvement has a crucial role to play in the further development of the biodegradable polymers market. Biodegradable polymers can be found in a wide range of end use markets. Continued progress in terms of product development and cost reduction will be required before they can effectively compete with conventional plastics for mainstream applications. And, the addition of natural fibers can lead to physical properties improvement and also can diminish cost. Additionally, it will reduce the amount of agribusiness waste disposal in the environment. In Brazil, coconut production is around 1.5 billion fruits by year in a cultivated area of 2.7 million hectares, but the coconut husk fiber has not been used much for industrial applications. Moreover, when considering an application in the medical field, it is necessary that the products are sterilized and, ionizing radiation is widely used to sterilize medical and surgical devices. In this work, it was studied blends and composites based on two commercial polymers: poly (-caprolactone), PCL, and poly (lactic acid), PLLA, and coconut fiber. Those polymers are biodegradable as well as biocompatible, so it is important to know the effect of ionizing radiation in these materials. Samples were irradiated with gamma rays from $^{60}Co$ source and, electron beam from Dynamitron Accelerator, with radiation doses ranging from 10 kGy up to 1 MGy. The non-irradiated and irradiated samples were studied using several analytical techniques and characterization assays that allowed understanding their properties in order to enable their application as precursors for medical and surgical devices. Thermal processing used to obtain composites and previous acetylation by chemical treatment of coconut fibers contributed to the bioburden reduction. Furthermore, reducing initial bioburden it was possible to diminish radiation doses needed to perform sterilization. Enzymatic and soil degradation were not negatively affected by radiation processing. Even though fiber incorporation to the polymer blend slightly reduced degradation process, composites continued degrading through time. Artifacts produced by means of the materials studied here can be radiation processed with doses up to 100 kGy without prejudice of their biodegradability.

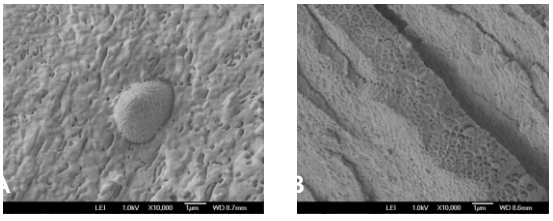


Figure 12. SEM micrographs of composite with 10% non chemically treated coconut fiber: A) non irradiated; B) irradiated with 100 kGy, cryogenic fractured.

**Modification and preparation of polymeric nanogels by ionizing radiation**

Hydrophilic polymers are widely used in medicine both in soluble and insoluble (hydrogel) forms. Water-soluble polymers have been used in the clinics and/or clinical trials for the modification of proteins, modification of liposomes, surface modification of biomaterials, and as carriers of drugs, genes, and oligonucleotides. The radiation-induced synthesis of PVP nanogels based on intramolecular crosslinking has been recently established. Such materials acquire specific properties that led to a great deal of potential applications, including drug-delivery systems, nanosensors, nanoreactors, and bio-mimetic mechanical devices. In this work we developed poly(vinyl-1-pyrrolidone) nanogels, synthesized by ionizing radiation. Additionally we aimed to produce PVP albumin conjugate system for biomedical applications. On this account, PVP was irradiated in gamma and electron beam sources using cosolvent system (water/acetone) at room temperature. Bovine serum albumin was incorporated after nanogel formation, by ressuspension of the lyophilized nanogel using saturated protein solution. The produced systems were characterized by means of particle size, using dynamic light scattering, nanostructure images were obtained by scanning electron microscopy. Under the evaluated conditions it was possible to synthetize nanostructured PVP hydrogels around 30-80nm hydrodynamic radius. The addition of protein to the system conferred distinct thermal profiles and led to changes in the overall structure of the system. Applications of the developed polymer albumin conjugate involve drug delivery systems with enhanced biological compatibility and specific site delivery.
spectroscopy (XPS), thermal analysis, and scanning electron microscopy (SEM). Cumyl dithiobenzoate (CDB) mediated RAFT polymerization of GMA revealed the difficulty of controlling the polymerization of GMA due to high crosslinking tendency of this monomer under γ-irradiation.

**Controlled radical polymerization and grafting onto polymeric substrates using ionizing radiation**

Modifying the surface properties of polymers is not only desirable but also vital to control the surface interactions and responses which are required especially in adsorption, separation, and biotechnology applications. The grafting technique can be improved and yield superior results when it is performed in conjunction with controlled radical polymerization (CRP) techniques instead of conventional free-radical polymerization methods. The advent of CRP methods combining the inherent advantages of free-radical polymerization with that of living polymerization methods in their own way enabled the synthesis of well-defined, narrowly dispersed polymers with designed architectures and molecular weights. Among the CRP methods, the reversible addition–fragmentation chain transfer (RAFT) polymerization is considered as advantageous considering its applicability to most monomers that reacts through radical polymerization, compatibility with various reaction conditions and simplicity of execution compared to competitive techniques. In addition, RAFT mechanism can successfully be utilized in radiation-induced polymerizations which enable the synthesis of tunable surfaces in a controlled manner by a one-step method that leads to stable and strong bonding between the surface and the grafted polymer under mild conditions without any pre-functionalization step. Nonwoven fabrics are porous materials with great surface area and they have potential for use in separation and purification of a large range of materials from metal ions to biomolecules after proper surface activation and modification. Considering their inherent characteristics, PHEMA grafted PE/PP nonwoven copolymers may have potential use especially in biomedical applications. The synthesized nonwoven fabrics may also lead to more complex structures via further chain growth or block extension by subsequent addition of monomer due to post-polymerization activity of their chain ends as grafting was performed in the presence of so-called RAFT agents. The irradiation was performed at room temperature in N2 atmosphere by using a Gammacell 220 $^{60}$Co source at absorbed doses from 5 up to 16 kGy for RAFT mediated grafting. It was possible to synthesize PHEMA grafted PE/PP nonwoven fabric via γ-initiated RAFT mediated graft copolymerization technique. The grafting process follows the model of front mechanism that is favourable for obtaining higher degree of grafting values in a controlled manner when a substrate suitable for this mechanism and a rapidly polymerizing monomer are used. Cellulose is the most common organic polymer and a very important sustainable raw material. Over the last decade, research to utilize cellulose as a base for the development of new polymers has intensified. Esters and ethers of cellulose are used in coatings, films, membranes, controlled-release systems, and pharmaceuticals. One of the well-established methods to modify a substrate is grafting of a functional polymer onto the surface of the substrate. GMA was grafted from cellulose by the combination of radiation-induced initiation and the RAFT technique, leading to epoxy functionalized surfaces that enable further modifications. The effects of adsorbed dose, monomer concentration, and solvent choice on grafting yield were investigated at three different monomer/RAFT agent ratios. The synthesized copolymers with various graft ratios were characterized by ATR-FTIR spectroscopy, X-ray photoelectron spectroscopy (XPS), thermal analysis, and scanning electron microscopy (SEM). Cumyl dithiobenzoate (CDB) mediated RAFT polymerization of GMA revealed the difficulty of controlling the polymerization of GMA due to high crosslinking tendency of this monomer under γ-irradiation.

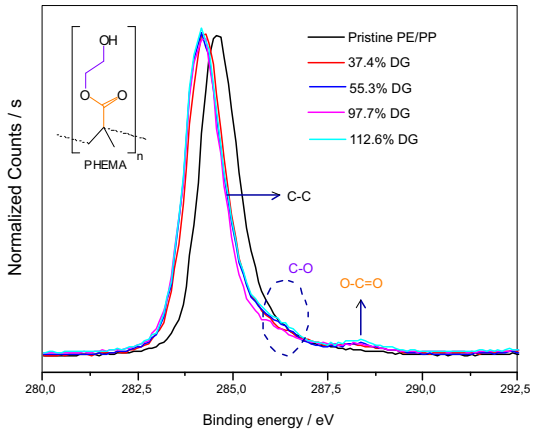



Figure 13. C1s XPS spectra for pristine PE/PP nonwoven fabric and PE/PP-*g*-PHEMA copolymers with various degree of grafting (DG).

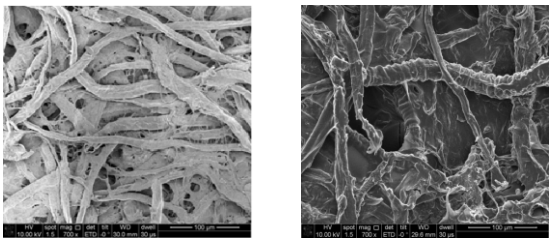


Figure 14. SEM images of (a) pristine cellulose, (b) cellulose-*g*-PGMA, 55% grafting.

**Development and applications of polymer, matrix composites, and nanocomposites by ionizing radiation**

The studies are focused on the development and modification of composite and nanocomposite based on natural and synthetic polymer matrix, micro and nanoparticle from natural resource such as, fiber residues from the Brazilian biodiversity, wastes from Brazilian agro-residues, and Brazilian natural clay, metal nanoparticles, graphene and also ionizing radiation treatment. The utilization of residues avoids waste through the reuse of materials that would otherwise have been discarded and can bring social and economic benefits for several regions of Brazil by generating jobs and preventing rural people from having to migrate to the city in search of better conditions of life. Based on the previous important questions the present research focuses at development of advanced food packaging materials and at development of new materials for applications in automotive industry.

**Styrene grafting onto several polymer types**
Physical parameters (vacuum, pressure of air or inert gas and temperature) influences on styrene grafting onto hydrocarbon and fluorinated polymers. Vacuum and temperature are determinant parameters to be considered in mutual radiation grafting besides the backbone polymer, monomer molecules and solvent. The optimization of these parameters for a specific polymer/monomer system contributes to a good performance and allows mutual radiation grafting to be an attractive technique even if it is performed in commercial accelerators. Also, the nature of process solvent influences the grafting yields: the mixture of styrene and protic polar solvents allow high degree of grafting. This behavior suggests that grafting process does not have dependence on swelling of the substrate, something that is expected when a non-polar substrate and a non-polar media are in contact. In this case, the grafting yield may be related to the free radical generation at protic polar solvent; these reactive specimens start the reaction on substrate surface to allow the accessibility of monomer species to active sites.

**Mechanical behavior of styrene grafted PVC films by electron beam irradiation**
Changes are observed in mechanical properties of styrene grafted PVC by electron beam irradiation using mutual and pre-irradiation methods when irradiation procedures are performed in atmosphere air or inert atmosphere and the irradiation conditions comprised doses from 10 kGy to 100 kGy and dose rates of 2.2 kGy/s and 22.4 kGy/s.

**Selective membranes by ionizing irradiation method**
Polymeric membranes are styrene grafted by irradiation methods and the obtained material is chemically modified to become aluminum selective. For this purpose, polymeric substrates like PVC (polyvinyl chloride) and PP (polypropylene) are styrene grafted mutually by gamma and electron beam irradiation. The modification process includes three basic reaction paths: Friedel-Crafts acylation, 2-methylanisole coupling and a final oxidation to achieve aluminum selectivity. The obtained product is a aluminum selective material where original membrane characteristics (physical shape and mechanical resistance) are conserved after such an aggressive treatment.


Figure 15. Physical aspect of the final product of aluminum selective membrane. (1) StyrenegraftedPP-1, with high yield of grafting (not chemically modified). (2) Chemically modified PP-1 (low yield - first step of modification). (3) Chemically modified PP-1 (high yields - first step of modification and grafting). (4) Chemically modified PP-2 (high yield for the first modification and low yield of grafting).

**Effect of gamma irradiation on caprolactam migration from multilayer polyamide 6 films into food simulants**
Gamma irradiation of multilayer polyamide 6 (PA-6) films on caprolactam migration from intended for cheese into water, 15 ethanol, olive oil, and 3 acetic acid simulants shows high migration rate (from 4.82 of caprolactam to 11.32 mg/kg PA-6 films) when compared to non-irradiated films (rate from 1.03 to 7.59 mg/kg). Irradiation causes no changes in caprolactam levels and these irradiated multilayer PA-6 films is in accordance with the requirements of the legislation for caprolactam migration.

**Polymerization of tilapia (*Oreochromis Niloticus*) skin by electron beam irradiation**
When tilapia skins are exposed to ionizing irradiation from electron beams under comprised doses of 20 kGy and 40 kGy and dose rates of 2.2 kGy/s and 7.4 kGy/s, the collagen fibers are disposed as a sheaf of straight filaments, that differ of collagen fibers randomically presented at non-irradiated in natura samples. Irradiated samples show high integrity and high tensile strength.

**Controlling bandgap energy and multivibronic modes of a Poly(2,5-thiophene-1,4-dialkoxyphenylene) derivative by gamma photons**
The influence of γ radiation on electronic, structural and vibrational properties of a poly(2,5-thiophene-1,4-dialkoxyphenylene), a photo luminescent material, is to come up with a new physical-chemical route to treat and increase conjugated polymers' efficiency.

**Ionizing radiation as optimization method for aluminum detection from drinking water samples**
The ionizing radiation is used as an advanced oxidation process (AOP), for sample pre-treatment before the analytic determination of total and dissolved aluminum by ICP-OES in drinking water samples from wells and spring source located at Billings dam region; the ionizing irradiation process applied as pre-treatment step in an analytical determination was an innovative procedure and it covered two kinds of sample:

1) standard water samples containing humic acid, that is the more common type of organic polymeric matter in ground water and

2) natural water samples from wells. Before irradiation, the spring source and wells' samples showed aluminum levels of 0.020 mg/l and 0.2 mg/l respectively; after irradiation, both samples showed a 8-fold increase of aluminum concentration. The irradiation process allowed the decreasing of the organic matter levels and the mineralization of these water samples contributing with unpublished data about the contents of aluminum.

**Cure of inks, paints, and varnishes by UV/EB technology and evaluation of its degradability**
The search for environmentally friendly materials is becoming one of the major focuses of research in the twenty-first century, considering the high level of pollution generated by the inadequate disposal of materials, especially polymers or plastics, in the environment. In addition, environmental legislation already in course in many countries limits the emission of volatile organic compounds (VOC) in the atmosphere. Thus, the technology of curing polymer coatings by radiation is based on the interaction of chemical system with the ultraviolet (UV) or electron beam (EB) incident radiation, forming reactive species capable of inducing polymerization reactions and cross-linking. In this technology, the organic solvents used to reduce the viscosity of the formulations are replaced by reactive monomers that remain in the cured product, providing no VOC emission. The dry/cured film is obtained at room temperature. However, the cured products are insoluble and infusible, increasing the degree of complexity for reprocessing, recycling, and required degradation.

**Gamma radiation effects ($^{60}$Co) into the main physical and chemical properties on packaging formed by paper and laminated plastic film, bound for sterilization of healthcare products**
Gamma radiation is one of the technologies applied for the sterilization of packaging systems containing products for health. During sterilization process it is critical that the properties of packages are maintained. In this study two samples of commercial pouch packaging comprised of surgical grade paper on one side and the other side multilayer plastic film were irradiated with gamma rays. The following doses were applied 25 kGy (1,57 kGy/h) and 50 kGy (1,48 kGy/h). One packaging sample was paper formed by softwood fibers and multilayer plastic film based on poly (ethylene terephthalate) (PET)/polyethylene (PE). The paper was the more radiation sensitive among the studied materials and radiation effects were more pronounced at brightness, pH, tearing resistance, bursting strength and tensile strength. Nonetheless, worst comparatively effects were noted

on the sample made by a mixture of softwood and hardwood fibers. The porosity of paper was enhanced by 50 kGy. In the case of plastic films, radiation effects on tensile strength was the most pronounced property for both samples. In the case of the packaging the sealing resistance decreased with radiation. The effects observed for the treatment at 50 kGy were more pronounced when compared to 25 kGy. This last is the dose which is usually applied to sterilize health products. A dosimetry study was performed during irradiation at 25 kGy, 40 kGy and 50 kGy and its importance may be reported by the average dose variation 20%.

**Reduction of environmental impact generated by radiation-cured print inks on post-consuming biodegradable plastic packaging**
Research is being done in order to improve the degradability of cured films disposed in the environment. This project aims to evaluate the influence of pro-degrading agents on printing ink formulations, applied on different polymeric substrates or plastic packaging and cured by UV or EB radiation. The degradability of these cured films is being evaluated by the changes in their thermal, mechanical, rheological, and morphological properties during natural weathering and accelerated ageing, as well as biodegradation in simulated soil.

## Preservation of cultural heritage

**Application of gamma radiation on recovery of paper infected by gungi and bacteria: the flood of São Luiz do Paraitinga**
São Luiz do Paraitinga, an 18th-century city located in São Paulo State, Brazil, is considered by the country as cultural and historical heritage. On January 1st, 2010, the city was hit by a devastating flood which resulted in the loss and destruction of historical and public buildings, monuments and houses. The referred places were highly damaged in their structures and inhabitants lost nearly all belongings, including identities and personal documents. The Nucleus of Conservation of the São Paulo State Public Archive (APESP) and the Nucleus of Conservation and Restoration Edson Motta - laboratory of the National Service for Industrial Apprenticeship (NUCLEM-SENAI), partnered with the aim of saving and preserving documents and other materials.

After a very careful cleaning and drying process, many of contaminated paper made property were submitted to a low dose of gamma radiation, in a compact Cobalt-60 irradiator from the Radiation Technology Centre of the Nuclear and Energy Research Institute, CTR-IPEN, to kill microorganisms. In this context, some books which were affected by flood and did not have any information registered indicating ownership were used as samples in studies, as well as other real objects. Determining fungus and bacterial species, comparing the characteristics of paper samples and the bio burden level before and after the submission to cobalt-60 gamma rays and then comparing the results with artificially aged paper-made materials is the purpose of a ScD thesis.

Figure 16. City hall (Photo by Fernanda Auada).

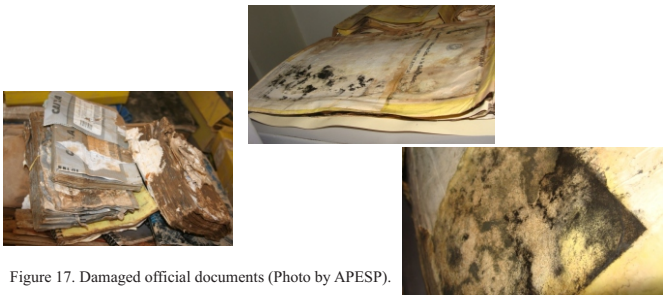


Figure 17. Damaged official documents (Photo by APESP).

Figure 18. Cleaning and drying process (Photo by APESP).

**Application of gamma radiation for recovery of manuscript with iron-gall ink**
Great part of the documentation kept under the custody of archives and private collections was produced with iron-gall ink on both rag and modern paper. The iron-gall ink was used almost exclusively in the western civilization from the Middle Age until the 20th century, on official documents, drawings, maps, pictures and other manuscripts.

Nowadays, the conservation of this type of paper-based materials presents several issues, especially in countries like Brazil, due to the great variety of climates, including tropical, with high average temperature and humidity.

The aim of this work is to study the effects of the gamma ray from Cobalt-60 source in irradiation treatments for disinfestation or disinfection purpose of collections and cultural items of both public and private property containing traces of iron-gall ink without promoting or increasing the corrosion process of paper by the referred ink.

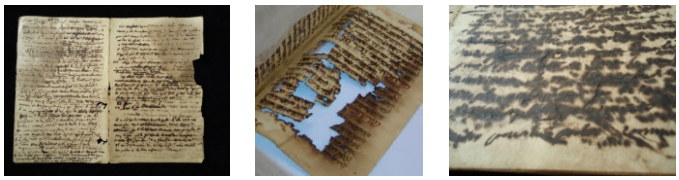


Figure 19. Manuscripts with iron-gall ink in degraded status (Photos by Gabriela M. Bakiewicz).

## Industrials processes application

**Industrial process equipment troubleshooting with imaging technique improved gamma-ray absorption scans**
Column gamma scan is one of the most common nuclear techniques on troubleshooting industrial process equipments like distillation columns and reactors. With a very simple concept, the technique is easy to implement: consisting basically on a sealed radioactive source that moves parallel to a NaI(Tl) detector resulting on a 1D unidirectional density profile of the equipment. Searching for a competitive edge the industry has been long developing solutions to achieve better results. On the last decades, significant development has been done with the advent of new hardware, electronics, portable computers, and software. Continuous scanning and wireless detection systems are examples of successful field solutions, while new software's aid on reporting and data presentations. However the type and quality of the results itself has not dramatically changed since its beginning. A scan profile is simple to understand, although the process to build it can be very complex as it requires a specific blend of knowledge and abilities. Process engineering, chemical engineering, internal hydraulic project, nuclear engineering, and field abilities are pre requisites for of any scan specialist. Correct data gathering, interpretation and reporting are abilities often difficult to match or requires a long time of training. The industry faces a similar difficult on the customer side, as it is always necessary to train end users to understand a report and how to use its best. This scientific work, initially developed as a Nuclear Science Master degree project, describes our effort on developing a new approach on the gamma column scan test using image reconstruction techniques that would result on a two dimensional graphic image rather than a XY plot. Direct and easier to understand, a report with graphic images would be also be accessible to a wider audience, not limited to the customers experienced with gamma scan interpretation. The

innovating technology, resulted on a patent register at Instituto Nacional de Propriedade Industrial (INPI), and recently received the 2013 Petrobras Technology Award, for Master Degree projects on refining and petrochemical area.

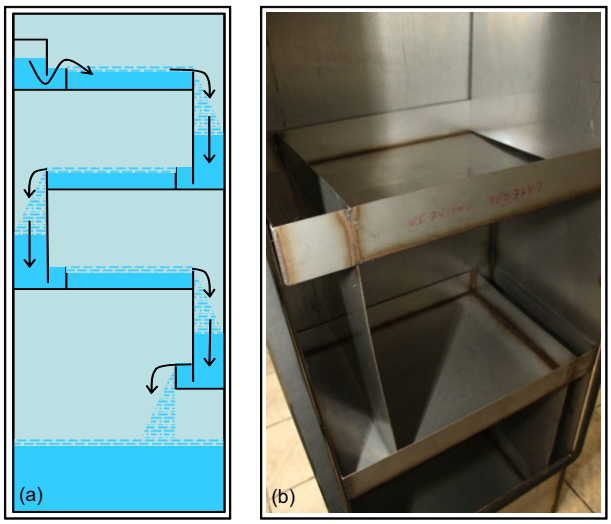



Figure 20. Liquid flow path scketch in a one pass trayed column (a) and detail of the experimental trayed column built (b).

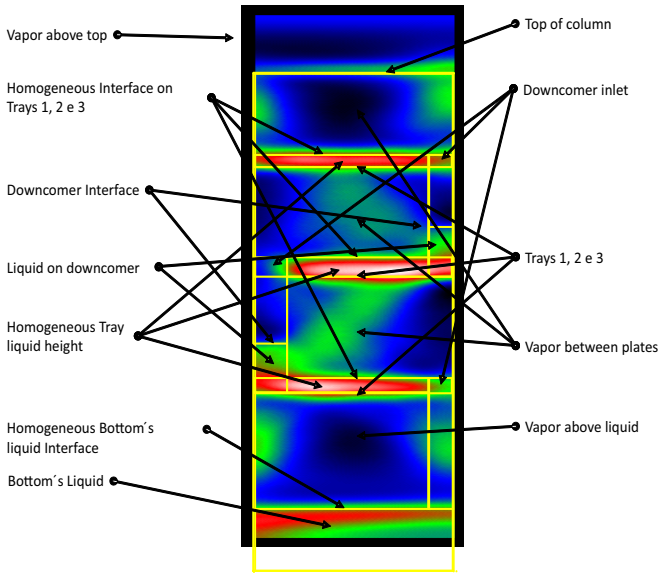



Figure 21. Mechanical and process diagnostics features observed on a tomographic image.

**Sealed source production for gammagraphy and industrial process control**

Radioactive sealed sources production for radiography and industrial process control. The gamma writing is an important non-destructive technique to analyze metallic components from small to large ones that need high performance and security in operation. Then on-existence of internal failures is checked by gamma rays radiography, because of its great penetration characteristics that allows obtaining the photographic record of failures. This non-destructive analysis is used for quality control of welded components in chemical, nuclear, and mechanical industries, such as pipelines, turbines, reservoirs, and pressure vessels. According to the International Atomic Energy Agency (IAEA) information, the petrochemical and chemical process industries are the mains users and beneficiaries of the radioisotope technology. Radioisotope techniques are very competitive and are largely applied for troubleshooting and process analysis of technically complex, continuously operating industrial plants. Due to this fact, the application of sealed sources becomes more diversified, including for gamma scanning of columns, vessels and pipes, level and interface detection. Since 1983, the Radiation Technology Center (CTR) has supplied industrial gamma sealed sources to more than 25 customers in Brazil and other countries in Latin America and Caribbean. Annually, the laboratory produces 280 sealed sources, with activities ranging from 740 GBq (20 Ci) to 4,444 GBq (120 Ci) of Iridium-192 and from 0.37 GBq (10 mCi) to 18.49 Gbq (500 mCi) of Cobalt-60. The CTR has made 290 inspections in irradiators, command cables and guide pipes annually and also Selenium-75 sources loading services. These supplies allow taking more than 100,000 radiographies per year. The principal CTR' customers are Arctest, ASNDT, Brasitest,CBC, JLM, Confab, Nuclep, TopCheck, Gamatron, Qualitec, Engisa, Capaz, Endlabor, NDT, Sperj, Polyteste, Usiminas, Real WDR, Nuclep, Radiolab,Voigth Hydro, Metaltec, Startec, Accend and Sertech.

**Use of radioisotopes as tracers in the environmental and industrial process control**

Radioactive tracers, as bromine 82, and dye tracer, as rhodamine WT, are applied to a grounded pipe flow rate measurements. Flow rate order of magnitude 0.1 $m^3$/s up to 3.5 $m^3$/s. Radioactive tracer, iodine 131, applications for mean residence time determinations in tank and digesters of domestic and industrial wastewater treatment plants. Volume order of magnitude: 7,000 $m^3$ up to 12,000 $m^3$.

**Gemstones enhancement using gamma radiation**

It's estimated 70% of the world's production of gemstones has been submitted to enhancement process and has consequently increased in commercial value. Thus, the CTR performs research of process to induce or intensify the color in several gemstones using gamma radiation. Enhancement services of colorless Brazilian quartz and other types of precious stones has been performed in the Gamma Multipurpose Irradiator for the companies Murta Gems Trade Gemstones (Minas Gerais State), Stoll Precious Stones of Brazil (Rio Grande do Sul State), Legep Mining and Geosciences Institute of Sao Paulo University (Sao Paulo State). The figures 22 and 23 show colored varieties of Brazilian quartz obtained to enhancement processes using gamma radiation and heating.

Figure 22. Colored varieties of treated quartz.

Figure 23. Rough and cut green gold irradiated quartz (70-100 kGy).

## Environmental recovery

**Treatment of Industrial effluent from industrial automotive and refinish paints for reuse**

The reuse of the treated effluent is one of the possibilities that should be considered in order to minimize the environmental impacts and to reduce the use of natural resources. Chemical oxidation processes are promising for degradation of toxic organic compounds. It was studied the effluent from the manufacture of automotive, automotive refinish and industrial paints. The methodology used was a case study, developed through the electron beam processing of these effluents. The main results have shown an average reduction of about 10% of Chemical Oxygen Demand, COD and about 25% of Biochemical Oxygen Demand, BOD. The final effluent standards set by legal requirements for disposal of the body in the river or reuse in industrial application.

**Application of ecotoxicity and radiation for the improvement of aquatic environment**

The Environmental Assay Laboratory, LEBA is in charge of toxicity assays aiming acute and chronic effects of pollutants and they are useful for the assessment of toxic charge in effluents. It is also developed ionizing radiation technology application for complex effluents in order to reduce toxicity which most often are correlated to

the degradation of organics in waters. The combining of both ecotoxicology and radiation technology may guarantee that radiation may reduce toxicity offering a safe technology or its combined processes for complex effluent.

Several studies were carried out for real effluents, including Sabesp, Petrobras and Chemical industries. Surfactants were also studied, and very low dose was required for controlling detergents in water and wastewater. Nowadays part of the research includes the radiation effects in pharmaceuticals as residues contained in wastewater. All irradiations are performed at a Dynamic Electron Beam Accelerator.

In collaboration with some other groups which study alternative treatments for wastewater LEBA participate of their work applying and developing suitable biological assays for measuring the efficiency of treatment developing processes such as MBBR and other POAS. Bellow are presented the living organisms applied during ecotoxicity studies and they are reared at LEBA. The Hyalella azteca is a organism very related to the bottom of Rivers and is used for studies related to sediments in order to amplify the information when Rivers are monitored. The intention of c) Figure is to give attention to part of the so called emergent pollutants well represented by the residues of pharmaceuticals today detected at wastewaters and even in water reservoirs for public supply.

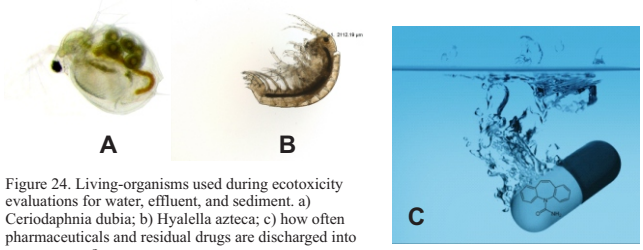



Figure 24. Living-organisms used during ecotoxicity evaluations for water, effluent, and sediment. a) Ceriodaphnia dubia; b) Hyalella azteca; c) how often pharmaceuticals and residual drugs are discharged into sewer system?

**Assessment of toxicity in water and sediment from Cubatão River-SP**

The Cubatão district is one of the largest industrial centers of Brazil. The usual discharge of industrial effluents and domestic sewage into Cubatão and its tributaries ended up causing serious waterways degradation. Cubatão River Basin is located between São Paulo and Baixada Santista (coast), covering approximately 177km$^2$ areas. Cubatão River as the main water source for the region, suppling water to Cubatão and its industrial area, and also to Santos, São Vicente and partially to Praia Grande and Guarujá municipalities. The objective of this study was to assess the toxicity for aquatic organisms concerning water and sediment sampled at Cubatão and at two tributaries (Perequê and Pilões). *Ceriodaphnia dubia* and *Vibrio fischeri* were used for evaluation of water effects while *Hyalella azteca* were exposed to the sediments. Biometric analyses were performed on *Hyalella azteca*. Furthermore, chemical identification by Chromatography and Neutron Activation Analysis were carried out in sediment samples. Through *V. fischeri* toxicity response it could be noted signs of effects once the EC(I)50 ranged from 31.25% up to 71.61%. *C. dubia* results were negative to the same samples, based on statistical analysis (test "t" for bioequivalence). Through acute toxicity responses when H. *azteca* was exposed to sediments, toxicity was identified in samples from P2 and P5 (2nd and 4th campaigns): mortality exceeding 50% of exposed organisms. The biometric analysis for the *H. azteca* growth showed lower values for organisms exposed to sediments from P4 and P5. Chemical analysis evidenced endrin, dibenzo(a, h) anthracene and anthracene at sediments from P5, values which are not in accordance with the Conama 344/04.

**Assessment of toxicity and genotoxicity of the reactive azo dyes Remazol Black B and Remazol Orange 3R and effectiveness of electron beam irradiation in the reduction of color and toxic effects**

The main impact caused by textile effluents is the deterioration of the receiving water body with the introduction of anthropogenic compounds that can disrupt the local ecosystem and its use to public supply. The reactive azo dyes are the main colors used in the industry for dyeing of cotton in Brazil and worldwide. The dyes discarded without treatment in the water body can cause aesthetic modifications, alter photosynthesis and gas solubility, as well as being toxic and genotoxic. The main objectives of this study were to evaluate the toxicity and genotoxicity of two reactive azo dyes (Remazol Black B and Remazol Orange 3R) and the percentage of color and toxicity reduction after the use of electron beam radiation. The acute toxicity assays performed with *Vibrio fischeri*, *Daphnia similis* and *Biomphalaria glabrata* showed different response patterns for dyes. The different chemical forms of dyes were slightly toxic to *Vibrio fischeri* and only the RPB dye (vinylsulphone) was toxic ($EC50_{15min}$ = 6,23 mg $L^{-1}$). In tests with *Daphnia similis*, the dye RPB was slightly toxic in its patern form, sulphatoethylsulphone, (CE5048h = 91,25 mg L-1) and showed no toxicity in other chemical forms. However, the RA3R dye was toxic to the dafnids and the vinylsulphone form very toxic ($EC50_{48h}$ = 0,54 mg $L^{-1}$). No toxicity was observed in *Biomphalaria glabrata* assays. Chronic toxicity was assessed with the organism *Ceriodaphnia dubia* and the NOEC and OEC values of RPB dye (sulphatoethylsulphone) were 12.5 and 25 mg $L^{-1}$, respectively. After hydrolysis (vinylsulphone and hydroxyethylsulphone) of this dye the values obtained from NOEC and OEC were two times higher, 25 and 50 mg $L^{-1}$, respectively. There was no chronic effect for the R3AR dye and its chemical forms to *C. dubia*, with NOEC and OEC values above 100 mg $L^{-1}$. The comet assay adapted to hemocytes of *Biomphalaria glabrata* was used to assess the genotoxicity of the dyes. The RPB dye was genotoxic at highest concentrations (1 and 2 g $L^{-1}$), with quantitative values of DNA damage equal to 117 and 112 and the R3AR dye was not genotoxic. After irradiation of the RPB dye, only a dose of 10 kGy reduced 58% of the acute toxicity measured with *Vibrio fischeri*. For the other doses there was no significant reduction, as well as with *Daphnia similis*, where the values of $EC50_{48h}$ obtained were smaller than the non-irradiated dye. The R3AR dye showed better decreased toxicity after radiation when compared with the RPB, with reductions of 80.85% (*V. fischeri*) and 71.33% (*D. similis*) with 10 kGy. Probably due to its simple chemical structure and high levels of acute toxicity of the non irradiated dye.

**Study of the response from snails *Biomphalaria glabrata* (Say, 1818) facing stressor environmental stimuli, with a focus on protein HSP70**

Molluscs have been employed as bioindicators in studies of environmental stress. The HSP70 protein is a molecule of 70 kDa, inside a family of proteins with role in maintaining homeostasis in the living being: the Heat Shock Proteins (HSPs), and is one of the most studied molecules as a potential biomarker for environmental injury indicating stress and protecting the protein damage in organisms. In this work, it was characterized the protein HSP70 in *B. glabrata* by Wiestern blotting aiming its employment in future environmental applications. To this purpose, 5-6 months old snails, with shell diameter of 14,4 (±1,7) mm, were exposed to heat and to cadmium chloride ($CdCl_2$) in order to verify the response of this protein in the presence of such different stresses. Animals were dissected to investigate induction of HSP70. It was observed that exposition to sublethal temperatures improved the resistance of snails *B. glabrata* to lethal temperature of 42ºC. Previous sublethal exposure to heat at 33°C and to $CdCl_2$ at 0.22 ppm improved the survival of snails *B. glabrata* to a lethal concentration of $CdCl_2$ (0.7 ppm) and to a lethal temperature (42ºC), respectively. The findings pointed to a possible role of HSP70 protein in this process, as could be seen on the Western blot. The digestive gland was the most responsive tissue to stress, regarding the HSP70 protein induction, compared with heat/foot and ovotestis. It was found an induction peak of HSP70 in snails *B. glabrata* after 48 hours of exposition to heat at 33°C, and after 96 hours of exposition to $CdCl_2$ at 0.22 ppm.

## Energy production

**Radiation effect on structure and composition of sugarcane bagasse**

The structural and chemical modifications produced by ionizing radiation in the sugarcane bagasse are very important matter to be included in the second generation energy production and it depends on the combination of pretreatment technologies to transform these modifications into bioethanol production growth. The industrial

application of electron beam accelerator on the second generation process is a challenging task and very feasible since the equipment could take part in the first generation installation. The radiation processing promotes an increase in the soluble portion that is related to hemicellulose and cellulose cleavage, and cellulose with high molecular weight (alpha) presented a total reduction. It is important to point out that the changes observed in the cellulose suggest some effects on the lignin structure, since the cellulose is protected by lignin and hemicelluloses. The obtained results show that radiation interacts initially on the surface of hemicelluloses liberating the arabinose, and then act on the xylose polymers. The main byproduct liberated is acetic acid originated from the deacetilation of hemicelluloses; the removal of this acetyl group enhances the accessibility of the enzyme to the cellulose and can increase the enzymatic hydrolysis. This sequence of radiation interaction probably happens due to the location of xylose in the backbone of arabinoxylan, while arabinose is located in the branches of the macromolecules where the glycosidic bonds are easier to hydrolyze.

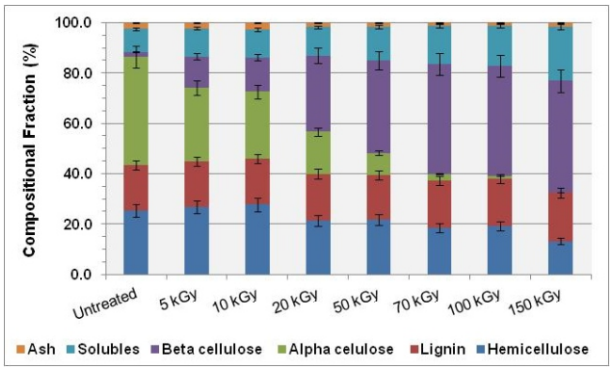



Figure 25. Compositional fraction of sugarcane bagasse untreated and irradiated in different absorbed doses.

**Radiation effect on enzymatic hydrolysis of cellulose**

The enzymatic hydrolysis were done in the Sugarcane Technology Center, using a commercial *Trichoderma reesei* cellulase preparation (Celluclast 1.5 L), kindly supplied by Novozymes (Bagsvaerd, Denmark). The enzymatic conversion yield of cellulose to glucose increased 50% with 20 kGy of absorbed dose. In an additional experiment applying absorbed doses up to 500 kGy, the conversion yield of cellulose to glucose did not increase for doses higher than 50 kGy. One reason for these results is the degradation of glucose by radiation and the inhibitory products formation.

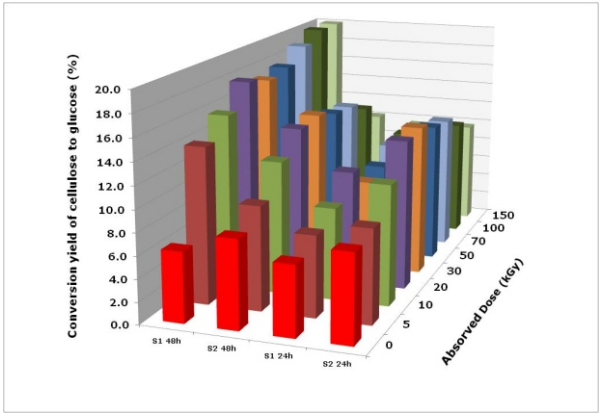



Figure 26. Conversion yield of cellulose to glucose in two sugarcane bagasse samples (S1 and S2) related to the absorbed doses after irradiation and enzymatic hydrolysis (24 and 48h).

**Radiation combined with hydrothermal treatment**

The hydrothermal hydrolysis of sugarcane bagasse at 180°C after irradiation with 50 kGy show a total reduction in oligosaccharides, liberating mainly xylose. However, the presence of formic acid and furfural, after 40 minutes of thermal treatment, mean that xylose and glucose are decomposed just after their liberation from hemicelluloses and cellulose. With the addition of diluted acid, the same amount of xylose is liberated as before, reducing the time from 40-10 minutes and the absorbed dose 50–10 kGy. In Fig. 27 is showed the increase in solubility that is proportional to the radiation dose and hydrolysis time; otherwise, radiation processing is more important when the samples were treated with thermal rather than acid hydrolysis. Considering only irradiation there is an increase of 16% in solubility, applying 150 kGy. Taking into account only the thermal hydrolysis for 10 minutes an increase of 22.7% can be observed and with the addition of dilute acid, the solubility rate increase to 42.2 %. Considering the solubility of samples non irradiated and irradiated at 150 kGy, the acid hydrolysis presented an increase of 1%, 3% and 6% for 10, 20 and 30 minutes, respectively, while thermal hydrolysis show 13%, 11% and 3% for 10, 20 and 40 minutes, respectively.

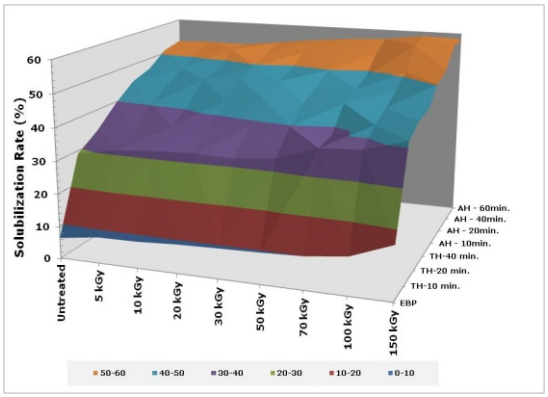



Figure 27. Sugarcane Bagasse Solubilization after Electron Beam Processing (EBP) Followed by Thermal (TH) and Acid Treatment (AH).

**Radiation combined with hydrothermal treatment and enzymatic hydrolysis**

The conversion of hemicelluloses reached 42% after thermal treatment by 40 minutes for sugarcane bagasse irradiated with 50 kGy. After the addition of diluted sulfuric acid (0.1% v/v), almost the totality of hemicellulose is converted in xylose and byproducts, mainly furfural. The enzymatic conversion yield of cellulose reached 72% in samples irradiated with 50 kGy and 60 min. of thermal treatment. When dilute sulfuric acid was added, it was observed an increase in the cellulose conversion, however the time was reduced, and the higher value (74%) was reached in 40 minutes of diluted acid treatment and 24 h of enzymatic hydrolysis (Fig. 28).

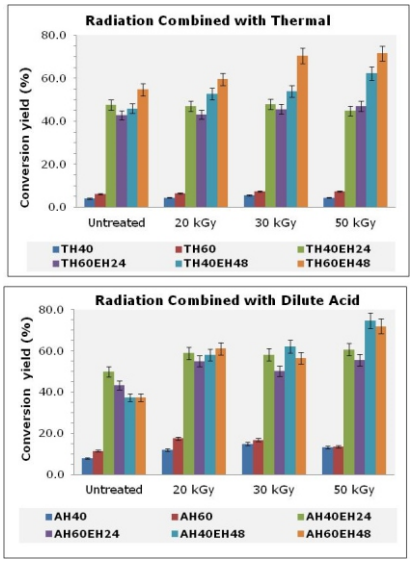



Figure 28. Enzymatic hydrolysis yield of cellulose after Electron Beam Processing (EBP) Followed by Thermal (TH) and Acid Treatment (AH).

**Electron beam application for regeneration of catalysts used in refinery cracking units**

A catalyst is a substance that alters the rate of a reaction. The process of catalysis is essential to the modern day manufacturing industry, mainly in Fluid Catalytic Cracking Process (FCC) units. However, long-term exploitation of oil and gas processing catalysts leads to formation of carbon- and sulfur-containing structures of coke and dense products on the catalyst surface. They block reactive catalyst sites and reduce the catalytic activity. The main advantage of radiation processing by electron beam (EB) and gamma rays is chain cracking reaction in crude oil. Otherwise, under exposure to ionize radiation, considerable structure modification of equilibrium silica-alumina catalyst from FCC process may occur, in addition to the removal of impurities.

Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRFS) analysis were used to characterize and evaluate effects of radiation processing on equilibrium catalysts purification. To evaluate and comprehend the reactive catalyst sites, Scanning Electron Microscopy (SEM) and particle size distribution analyses were carried out. Alternatively, Ni(Co)-Mo/$Al_2O_3$ catalyst is also used in the crude-oil processing, in a stage called Hidrocatalytic Cracking (HCC), the presence of Molybdenum and Cobalt adds high value to the catalyst. The use of Ni(Co)-Mo/$Al_2O_3$ catalyst is an example of material that, after thoroughly characterized, became framed as hazardous waste from the late 90's. This situation was maintained in the review published by the Environmental Protection Agency (EPA). When studying electron beam (EB) with higher energies is possible to induce the decomposition of supported Ni(Co)-Mo/$Al_2O_3$ sulfide catalyst and organic fragments of hydrogenation catalyst wastes and also recovery of noble materials such as cobalt and molybdenum, as well as, the study of catalyst impregnated with coke from the crude oil distillation on an industrial scale. To evaluate and comprehend the crystalline structures of Ni(Co)-Mo/$Al_2O_3$ and also FCC catalysts after gamma rays and electron beam irradiation, it will be necessary to carry out X-Ray Diffraction (XRD).

**Petroleum and diesel fuel desulfurization enhancement by ionizing radiation**

Hydrodesulphurization, HDS, is currently the most common method used by refineries to remove sulfur compounds from petroleum fractions. However, it is not highly effective for removing thiophenes compounds such as benzothiophene. Additionally, this process generates high costs for the oil industry. In the present work, ionizing radiation was used as an advanced oxidation process in order to enhance the removal of sulfur contents from petroleum and diesel fuel. Samples of crude oil and diesel fuel, without any pretreatment, were irradiated using a Radiation Dynamics Electron Beam Accelerator in batch systems at 30 kGy and 50 kGy absorbed doses. The sulfur compounds were extracted and then analyzed by gas chromatography associated to mass spectrometry, GCMS, and by gas chromatography coupled with flame ionization detector, GCFID. Furthermore, the petroleum and diesel fuel samples were analyzed by Fourier Transform Infrared Spectroscopy, FTIR, to detect chemical changes in sulfur compounds. It was observed a high efficiency of ionizing radiation on the degradation of sulfur compounds such as benzothiophene and benzenethiol and the formation of fragments, for instance 1,2-dimethylbenzene and toluene.

### Radiosterilization for tissue banks

In Latin America, the industrial level ionizing radiation sterilization has been used for more than three decades for foods and medical, pharmaceutical and cosmetics products are treated. Later, this activity was extended to the sterilization of human tissues for graft and reinforced in some countries by the technical cooperation and International Agency of Atomic Energy - IAEA financial support. In the last few years, preserved tissue allograft, such as bone, cartilage, skin, amnion and other not viable tissues, have been used in reconstructive surgery by many clinical specialties, like orthopedic and plastic surgery. The transmission risk of infectious diseases by allograft, however, is a constant concern. To this end, many steps should be taken, including tissue sterilization. This technique is used to minimize the immunogenicity, to kill bacteria and to reduce the contagious diseases transferring risk. As an example, the skin glycerol preservation has a bacteriostatic effect after certain time, on the other hand, skin sterilization by ionizing radiation may reduce the quarantine period for transplantation in patients, and their safety is considered excellent.

The ionizing radiation is a very efficient sterilization technique; nevertheless, its deployment is still contested since there are few data on its effects upon the tissue allograft. At the Radiation Technology Center, procedures using two sources of ionizing radiation for sterilization of human skin allograft, and to evaluate the skin after gamma and electron beam irradiation, were established. Besides implanting the irradiation services routine to the tissue banks of the country, the researchers developed irradiation devices for human tissues; implanted dosimetry procedures for irradiation processes control; implanted the quality warranty program for tissue irradiation; optimizing type and dose to be supplied according to the preservation process which the tissue was submitted.

Brazil was incorporated to the IAEA project in 1998 through the Clinical Hospital of Sao Paulo, where the Tissue Bank was installed and the Energetic and Nuclear Research Institute, where the tissues are being irradiated. Until 2012, Brazil was the coordinator of IAEA-ARCAL CVIII “Consolidation of Tissue Banks In Latin America And Radiation Sterilization of Tissue Allograft” project with 12 Latin-Americans countries participation and also, since 2010, our group participates in the CRP 16119 “Safety and optimization of radiation sterilization in tissue banking: studies on functional properties of irradiated tissue grafts”. The research group has been collaborating with the implementation of quality systems of the Tissue Banks, as well as with experimental and clinical applications of irradiated tissues. Tissue samples were submitted to 15, 25 and 50 kGy doses and the impact of the irradiation on the mechanical properties was evaluated through the analysis of stress-strain and the morphology was accomplished by ultra-structure studies, immune histology and others histological tests. Also in the current work, the studies using non destructives tests, like optical coherence tomography (OCT), with the Laser Applications Center collaboration, has been carried out.

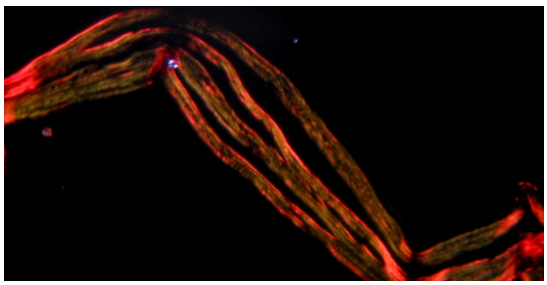


Figure 29. Visualization of collagen present in the amniotic membrane. Staining with Picrossirius.

### Development and production of radioactive sources for brachytherapy application

The number of prostate cancer cases in Brazil is increasing and only a small part of the patients are submitted to brachytherapy treatment using Iodine-125 radioactive seeds. Nowadays, these seeds are imported at a high cost, restricting this application. The local production of these radioactive sources became a priority in order to reduce the problems of prostate cancer management for end users. Such action will permit to spread the use to a larger number of patients. Due to such reasons, the Nuclear Energy Research Institute established a program, in order to produce Iodine-125 radioactive seeds. In brachytherapy, small seeds with Iodine-125 are implanted into the prostate to irradiate the tumor. The Iodine-125 seeds consist of a welded titanium capsule (0.8 mm diameter and 4.5 mm length) containing Iodine-125 adsorbed onto a silver rod. During the project execution, the following methods were developed: the seed core (silver) cutting, the titanium tube cutting, the iodine immobilization through its deposition in silver substrate and the sealing of the seeds through welding process, so that the classification of the seeds, as sealed sources, and the leakage tests can be done according to the international norms. In the moment, the routine production line is settling up. The production line consists in three gloves-boxes. In the first one the Iodine-125 will be adsorbed in the silver core. In the second one, the titanium tube will be sealed. And finally, in the third one, all the assurance tests will be carried out. All the automation process of the welding glove and the quality control glove are finished.

**Methods for Iodine-125 deposition in silver substrate**
Among the different ways to treat prostate cancer, brachytherapy with Iodine-125 seeds is an option that provides good results and fewer side effects. In the present study several methods of deposition of radioactive iodine in a silver substrate were compared in order to choose the most suitable alternative for the routine production to be implemented at IPEN's laboratory. The methodology used was chosen based on the available infrastructure and experience of the researchers present. The better method will be implemented in the IPEN's laboratory for brachytherapy sources production.

**Development of methodology for the synthesis of Poly(Lactic Acid-Co-Glycolic Acid) for use in the production of radioactive sources**
Iodine-125 seeds can be placed loose or stranded in bioabsorbable polymers. Stranded seeds show some advantages, since they reduce the rate of seed migration, an event that could affect the dosimetry of the prostate and cause unnecessary damage to healthy tissues or organs. For Iodine-125 stranded seeds, polyglactin 910 (poly(lactic-co-glycolic acid)) (PLGA), with a coverage of polyglactin 370 (Vicryl ®) is used. It was purposed in this project, the study and development of the synthesis methodology for PLGA via ring-opening polymerization, as well as its characterization, with the objective of using the synthesized material to manufacture a material similar to RAPID Strand®. The results obtained show that it was possible to determine the optimal reaction parameters (time and temperature) for PLGA in 80/20 (lactide/glycolide) ratio. Using a temperature of 110° C and reaction time of 24h, a yield of 86% was obtained, and increasing the reaction time to 72 hours, the yield was higher than 90%. The molecular mass values obtained from the samples are still very low compared to those obtained by other authors in the literature (about 20%). Failures in the sealing of vials, leaving them vulnerable to moisture and oxygen, or lack of an efficient stirring system might be possible explanations for these results. A suitable chemical reactor could solve the problem. Regarding polymer characterization, all techniques used not only confirmed the expected structure of the polymer, but also showed the highest proportion of lactide units compared to to glycolide units.

**Study and parameters survey for Iodine-125 source dosimetry to be applied in brachytherapy**
The objectives of this work are the development and the study of dosimetric procedures associates with the experimental acquisition of the useful parameters for the Iodine-125 dosimetric characterization and to evaluate if the developed procedures, in this work, have the basic conditions to determinate the dosimetric analysis, that are fundamental for clinical procedures. The dosimeters selected for the

analysis are the TLD-100 (LiF:Mg,Ti), initially these dosimeters were submitted for two selection steps to choose the dosimeters more reproducible for the dosimetric analysis. The two steps were the selection by the mass of the dosimeters and the reproducibility after four irradiation series in a Cobalt-60 irradiator (CTR-IPEN). After, the dosimeters were used to the irradiations with Iodine-125 seed, 6711 model, (GE-Healthcare). The irradiations and others analysis with Iodine-125 seeds yield the useful values for the determination of the parameters suggested by the AAPM (American Association of Physicists in Medicine): constant of dose rate, geometry function, dose radial function and anisotropy function. The results showed good agreement with the values published by the literature, for the same Iodine-125 model, this fact confirms that the realized parameters will be able to be used for the IPEN-CNEN Iodine-125 seeds dosimetry and quality control.

**Study and development of an iridium-192 seed for use in ophthalmic cancer**

Although ocular tumors are not among the cases with a higher incidence, they affect the population, especially children. The Institute of Energy and Nuclear Research (IPEN-CNEN/SP) in partnership with Escola Paulista de Medicina (UNIFESP), created a project to develop and implement a alternative treatment for ophthalmic cancer that use brachytherapy iridium-192 seeds. The project arose by reason of the Escola Paulista treat many cancer cases within the Unified Health System (SUS) and the research experience of sealed radioactive sources group at IPEN. The methodology was developed from the available infrastructure and the experience of researchers. The prototype seed presents with a core (192-iridium alloy of iridium-platinum) of 3.0 mm long sealed by a capsule of titanium of 0.8 mm outside diameter, 0.05 mm wall thickness, and 4,5mm long. This work aims to study and develop a seed of iridium-192 from a platinum-iridium alloy. No study on the fabrication of these seeds was found in available literature. It was created a methodology that involved: characterization of the material used in the core, creation of device for neutron activation irradiation, laser welding of the titanium coating and testing of quality control. The result, proved the feasibility of the method. As a suggestion for future work, studies regarding metrology and dosimetry of these sources should be carried out, for future implementation in national scope.

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### Honor Mention and Awards

The researcher Celina Lopes Duarte and her PhD student Fernando Codelo do Nascimento, has received the first place in 14th edition of the Prêmio ABRAFATI/PETROBRAS in Science of Paints with the work “Treatment of effluent from automotive paints, refinish and industrial with ionising radiation”. ABRAFATI-2012.

The master dissertation titled “Imaging of industrial equipment for the Profiling technique for gamma rays”, of Marcio Issamu Haraguchi guided by Wilson A. Parejo Calvo, was awarded at the 6th Edition of the Petrobras of Technology Engineer Antonio Seabra Moggi, in the category of master's degree in the area of Refining and Petrochemical Technology. The study was a collaboration of Dr. Hae Yong Kim of Escola Politécnica da USP, and Tricom technology.

The paper “Reversible Addition Fragmentation Chain Transfer (RAFT) Mediated Grafting of Glycidyl Methacrylate from Poly(ethylene)/poly(propylene) Nonwoven Fabric by Gamma Radiation” was awarded as the Best Poster at the 4th Asia Pacific Symposium on Radiation Chemistry, APSR-2012, Anhui, China, 2012. The authors are Murat Barsbay*, Yasko Kodama and Olgun Güven*. (*Haccetepe University, Turkey).

The researcher Celina Lopes Duarte and Manoel Nunes Mori, has received the first place in the 4° Top Ethanol Prize-2013, in Technological Innovation category, with the study entitled: “Pretreatment of sugarcane bagasse by irradiation with electron beam for ethanol production”. Project financed by AIEA and BIOEN-FAPESP.

The paper “RAFT mediated grafting of glycidyl methacrylate (GMA) to cellulose via-irradiation” was the poster awarded for an outstanding poster contribution at the International Meeting on Radiation Processing, IMRP 17, held in Shangai, China, 2013. The authors are Yasko Kodama, Murat Barsbay* and Olgun Güven*. (*Haccetepe University, Turkey).