Radiation Technologies: Processes and Products

Introduction

The activities carried out are essentially applied research and development on gamma radiation applications. Particular aspects of radiation sterilisation, polymer modification and detection of irradiated food are studied.

Radiation sterilisation is oriented to: good manufacturing practice of medical devices in conformity with EN and ISO standards; definition of microbiological parameters to the sterilisation of medical devices, pharmaceuticals and other products need to be sterile.

The BIOSTER *consortium* contract involving official institutions and industries is in progress. Specific protocols, technology transfer and training have been performed. Extensively reports of the work carried out were presented. An "audit" by AdI / PRAXIS XXI experts was successful passed. A university student has been graduated in Mathematics.

Work was published and presented to scientific meetings. Scientific and technological assistance to certification and normalisation institutions, and industry has been performed.

Polymer modification studies and basic characterisation techniques on the preparation of graft copolymers by gamma radiation have been continued. The optimisation of the technique for sealing samples prior to irradiation in controlled atmosphere was developed. This technique allows to increase our knowledge on the PE/HEMA system *versus* gamma radiation. Thermal characterisation techniques, DSC and TGA, were implemented.

The close collaboration with Prof. M. Helena Gil, University of Coimbra, has proceeded and reinforced.

Training has been carried out and work was published. A university student has prepared a dissertation thesis and obtained graduation in Chemistry.

An intercomparison study on **detection of irradiated** dried fruits using EPR technique have been carried out in collaboration with all partners of the EU contract "Establishment of Eastern Network of Laboratories for Identification of Irradiated Foodstuffs" The cooperation in that matter with INETI, INIA, ISA and IST has continued and put forward.

In the frame of the EU contract SMT4-CT-96-2077 a dosimetry intercomparison study is in progress.

The IAEA Research Contract on irradiation for disinfestation of dried fruits has been continued. Irradiation parameters in commercial practice for: figs, pine-nuts, raisins, and walnuts were determined. A new routine dosimeter the "clear Perspex", locally purchased, was assayed.

The work developed was published, presented to scientific meetings or described in progress reports. A university student has obtained graduation in Agro- Industries Engineering , other students are preparing dissertation theses for graduation, MSc and PhD.

Research Team

	Radiation Sterilisation	Polymers	Food Irradiation
Researchers Staff (1)	1 (1)	--	1 (1)
Research Students	2+ 3 [(c)]	1[(a)]	1[(b)]
University Students	1	1	3
MSc Student	--	--	1
Technicians Staff	1 + 1[(c)] + 2 [(d)]	--	--
Grantees	--	1[(d)]	--
Publications			
Journals –	1	1	3
Proceedings –	1	--	2
Internal Reports –	4	--	1
Theses:			
Lic.	1	1	1

( ) PhD or equivalent
[(a)] PRAXIS grant holder (PhD Student)
[(b)] On leave from INIA (PhD Student)
[(c)] PRAXIS grant holder
[(d)] ITN grant holder

10^3 PTE

Expenditure:	**14.142**
Missions:	2.328
Others Expenses:	8.129
Hardware & Software:	824
Other Equipment:	2.861

10^3 PTE

Funding:		**21.970**
OE/ITN	OF	548
External Projects:	1996	891 [(1)]
	1997	19.599
Others		932

[(1)] Funding not used in 1996

RADIATION STERILISATION

Biological Dosimeters *versus* Chemical Dosimeters: The Complement.

M. L. Botelho
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Abstract
The biological efficiency of the sterilisation process is usually described as the quality of inactivation effect that is produced on the exposed micro-organisms. The Pharmacopoeia and some of the International standards advise the use of indicators to confirm the sterilisation process efficiency. Although biological dosimeters can not replace the chemical or physical dosimeters, they are used to determine the biological efficiency due to the fact they estimate the inactivation effect on the micro-organisms i.e. gives directly the measurement in the systems that are under study.
Comparative studies between "biological" and "chemical" dosimeters are presented . These studies were developed in two kinds of products, ophthalmic suspension and ophthalmic ointment , the sterilisation dose was respectively 13 kGy and 25 kGy.
When the Grubb estimator was applied (α=0.05) to the values obtained through three different independent methods, the biological dosimeters, ceric/cerous and PMMA, proved that the biological dosimeters were the less precise. However, the statistical analysis obtained for the dose values using the chemical and biological systems showed very clear that there are not significant differences between them, (α=0.05).
The chemical and physical dosimetric systems characterise and validate the process (radiation sterilisation) in physical terms, i.e., giving a measure of the energy absorbed. However, it is also important at the initial stage of a sterilisation process to use biological dosimeters which can confirm its efficiency and reproducibility in biological terms , as this is the aim of a sterilisation process and the final objective for which it is designed.

Proceedings of "*Congresso Nacional de Microbiologia, Micro' 97*", Tomar, Portugal,
29 November-1 December, 1997, pp 68. (in portuguese).

Current Work

Study Case on Medical Devices Manufacturing - Bioburden Studies in/on Product. Gamma Sterilisation *vs* Sterilisation with Steam under Pressure

M.Luisa Botelho
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The purpose of this project is to develop and validate the methods to determine the microbiological parameters in medical devices prior to sterilisation.
The variation of the values of the initial count (No), both *inter* and *intra* lot is being analysed, taking into account the reproducibility of No. The main origins of contamination are being

studied, together with their contributions to the microbiological quality of the product prior to sterilisation.
In order to start the technology transfer two protocols were validated for the medical devices produced by the following companies: ophthalmic dressings / OFTALDER; absorbent surgical gauzes / B&V. The protocol of the surgical garments / FAPOMED is in progress. The dose distribution in products (ophthalmic dressings, absorbent surgical gauzes) was studied.
Three graduate students affiliated to the above referred companies were trained and have worked in the project (see Internal Reports).
The 1st Report was submitted and an audit was undertaken by scientific experts from AdI / PRAXIS XXI. The project passed the "audit report" successfully.
Two progress assessment meetings were performed at ITN with the *Consortium* Partners: Normalisation Institution (APORMED), Certification Institute (INFARMED), Industries (OFTALDER, B&V, FAPOMED).

Evaluation of Environmental Conditions

M. Luisa Botelho
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The microbiological environmental conditions at Haematology Ward - St. António dos Capuchos Hospital were evaluated by using the slit-sampler equipment which transfer determined amount of air directly to growth medium plates.
The total number of micro-organisms was estimated as well as the number of fungi. The principal contaminants were identified and classified in main groups.

Audit and Technical Committee

M. Luisa Botelho
Nuclear and Technological Institute, ITN, Physics, E. N., 2685 Sacavém, Portugal

An audit was developed to a company which performs environmental condition assays.
Expertise services were given as a member of the Technical Committee CT/870.

POLYMER MODIFICATION AND METHODS OF CHARACTERISATION

Current Work

Kinetic Studies of the Grafting Copolymerisation Reaction of HEMA onto PE, by Gamma Radiation

L.M. Ferreira[1], P. Pereira[1], M. E. Andrade[1] and M.H. Gil[2]

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[2]*Department of Chemical Engineering, Faculty of Science and Technology University of Coimbra, 3990 Coimbra, Portugal*

A technique for preparation the copolymer polyethylene-g.co-hydroxyethyl methacrylate (PE-g.co-HEMA), using gamma radiation as the energetic source for reaction initiation, has been developed at the Polymers Characterisation Laboratory (LCP) during the last few years. That new material seems to be a very promising support for the immobilisation of biological compounds.

The aim of these studies are the evaluation of the grafting kinetic parameters, for the production of graft copolymers in a reproducible way suitable for the immobilisation of enzymes.

Although, to establish the proper conditions to prepare the copolymer with the desired grafting yield, and with the desired mechanics and surface characteristics, we need to know the system evolution in different experimental conditions.

Therefore, the PE-g.co-HEMA system has been prepared under twelve different experimental conditions. These experimental conditions involve:

i. Different dose rates of irradiation (0.3 and 0.5 kGy/h);
ii. Different monomer concentrations (5, 10 and 15% (v/v));
iii. Different environments of irradiation (in the presence and in the absence of air).

The irradiation systems of (PE+HEMA) being studied are:

System Nº.	Irradiation Environment	Monomer Concentration (v/v in MeOH)	Dose Rate (kGy/h)
1	Presence of air	5%	0.3
2		10%	
3		15%	
4		5%	0.5
5		10%	
6		15%	
7	Absence of air	5%	0.3
8		10%	
9		15%	
10		5%	0.5
11		10%	
12		15%	

The available data allow to conclude that the grafting degree increases with the monomer concentration and with the absorbed dose. However, the yield of grafting (as well as the initial rate of the copolymerisation reaction) is higher in the absence of air.

Evaluation of the Cristalinity Lost in Based PE Graft Copolymers, Prepared by Gamma Irradiation, Using Calorimetric Techniques

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The recent work developed in the characterisation of the copolymer polyethylene-g.co-hydroxyethyl methacrylate (PE-g.co-HEMA), using calorimetric techniques: Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA), have shown to be very useful techniques in the evaluation of the thermal stability of this material.
The PE-g.co-HEMA samples have been prepared in different experimental conditions, using gamma radiation for the initiation of the copolymeric reaction.
The aim of these studies is to know the PE-g.co-HEMA profile behaviour with gamma radiation, as a function of the different experimental preparation conditions.
The available data allow to conclude at this point that:

i. The PE-g.co-HEMA thermal stability always decreases with the radiation absorbed dose;
ii. The graft of poly (HEMA) branches onto low density PE, leads to the matrix open, with the consequent cristalinity decreases of the polymeric backbone.

The thermal stability decreases of PE-g.co-HEMA is higher when the polymeric reagent system (PE+HEMA) is irradiated in the presence of oxygen. This fact is related with the increase of the degradation of LDPE when irradiated in these conditions.

DETECTION METHODS OF IRRADIATED FOODS AND DOSIMETRY

Certification of Reference Materials for the Quality Control of Major Element Determinations in Groundwater

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Abstract

Analyses of ground water are routinely performed by control laboratories within the European Union to monitor the levels of majors elements. The quality control of such determinations requires the use of certified reference materials which are representative of natural samples. However, the preparation and stabilisation of natural groundwater for their major element composition is difficult to achieve and materials simulating the mean composition of real samples often represent the best alternative. In order to investigate the feasibility of preparation and stabilisation of simulated groundwater samples, various tests were necessary prior to the production of a large batch of candidate reference materials. This paper presents the preparation of simulated groundwater reference materials and the different stabilisation procedures tested.

Fresenius J. Anal. Chem. **358** (1997) 574 - 580.

Dose Mapping of Dried Figs Treated by Gamma Radiation

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Abstract

The irradiation parameters of two varieties of dried figs were determined in a fixed position The Dose Uniformity (U=Dmax/Dmin) obtained for Fricke Dosimeter was 1.4 and for YR Gammachrome 1.3. The isodose curves were built using a geostatistical gridding method, the Krigging method.

Radiation Physics and Chemistry (in press).

Two Methods to Detect the Radiation Treatment on Ground Pepper: Viscosimetry and EPR

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[4]*Technical Superior Institute, IST, Av. Rovisco Pais, 1096 Lisboa Codex, Portugal*

Abstract

Pepper is a heavy contaminated spice originally from tropical countries. Many food-born diseases could be transmitted by food flavoured with pepper. Therefore, the microbiological decontamination is a must. Gamma radiation decontamination is a safe and effective process. Nevertheless, the consumers feel the necessity to have detection methods to identify foods submitted to a prior irradiation treatment.

Three methods to identify irradiated spices are currently applied: thermoluminescence, electronic paramagnetic resonance (EPR) and viscometry. In this paper the EPR and viscometry techniques applied to the case of pepper were studied. The protocols used to prepare the samples are described and the data obtained are presented.

Both methods are applicable for a qualitative identification of irradiated pepper. A quantitative or half-quantitative measurement of the absorbed dose by the pepper is also applicable with some reservations.

However, the EPR technique has presented limitations concerning the life time of the EPR signal. After the life time period the uncertainty of the data are not acceptable.

The viscometry technique is independent of time and does not present alterations on the rheological behaviour with the elapsed time.

The data obtained can contribute to the standardisation of the viscometry technique as is already the case for the EPR technique, standard EN 1787 / 1987 for foodstuffs containing cellulose.

Proceedings of the "3º Encontro de Química de Alimentos", "Escola Superior de Tecnologia", Algarve University, Faro, 23-26 March, 434-436 (1997). (in portuguese)

A Contribution to the Study of Structural Modifications on Dried Figs by Gamma Radiation

N. ***Ribeiro[1], I.M.N. Sousa[2], M.E. Andrade[1], I. Polónia[1], M.P. Esteves[3] and J. Empis[4].***

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Abstract

The ethylene oxide was the fumigant utilised to treat dried fruits, often infested with insects which decrease their commercial value. However, this fumigant has been forbidden in the EU since 1992.
Gamma radiation is a serious alternative to ethylene oxide as it is a reliable, efficient and environmental friendly process. If the technological parameters are correctly defined and applied the nutritive value of foodstuffs are not affected.
Portugal is a producer of figs and dried figs. Dried figs are consumed in the country and exported to third countries. Black dried figs from Torres Novas were selected to study potential modifications due gamma radiation treatment. The figs were irradiated with the absorbed doses of 1, 2.5, 5, 6 and 10 kGy..
To look for structural alterations in irradiated figs their hardness was measured by using a texturemeter. It was detected a decrease of the figs hardness when the absorbed dose was increasing, but after a storage period (35/60 days) these modifications were not measurable.
To a triangular panel has been asked the evaluation of the hardness parameter of irradiated dried figs. The panel could identify alterations in the figs hardness 10 days after the treatment. The panel also detected a relation between the increasing of the absorbed dose and the decreasing of the hardness. The figs irradiated with a dose of 6 kGy were easily identified. After the storage period these alterations were annulled and became undetectable.
The EPR technique to identify irradiated figs was explored using the figs' foot-stalk. It was possible to see that the intensity of the signal increases with the increment of the absorbed dose, but decays with time. In this study the signal has been detectable during 7 months a after irradiation. The potentialities of the EPR technique applied to dried figs need to be further studied.

Proceedings of the "3º Encontro de Química de Alimentos", "Escola Superior de Tecnologia", Algarve University, Faro, 23-26 March, 434-436 (1997). (in portuguese)

Current Work

Irradiation of Dried Fruits. Establishment of Irradiation Parameters

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The study to determine the irradiation parameters for disinfestation of dried fruits: figs, grapes, hazel-nuts and pine-nuts has continued. The dose distribution in commercial packaging was thoroughly studied. The locations of minimum absorbed dose (D_{min}) and of maximum absorbed dose D_{max} were defined. The absorbed dose uniformity ratio ($U = D_{max}/D_{min}$) was 1.2 up to 1.4 for the dried fruits studied. The isodose curves were drawn by using the automatic programme SURFER
Different dosimetric systems were tested. In a fixed position: the reference standard Fricke dosimeter (40 - 400 Gy) prepared and calibrated at ITN; the routine dosimeters: YR Gammachrome (100 - 3 000 Gy) purchased to Harwell Dosimeters / UK re-calibrated at ITN and PMMA-YL Dosimeter (50 - 1000 Gy) prepared and supplied by the Institute for Application of Atomic Energy, Beijing, China . For validation in commercial practice (running process) the routine dosimeters: Amber Perspex (3 000 - 30 000 Gy) purchased to Harwell Dosimeters / UK and recalibrated at ITN, Clear Perspex, purchased, at the local market, prepared and calibrated at ITN were utilised.
STERIN indicators of 150 Gy and 300 Gy were assayed to establish a simple and direct process for verification, by customs inspectors, of a prior irradiation treatment. These indicators change its aspect if the threshold dose has been received.
The performance of SERIN - 125 suggested that this colour indicator could properly be used for doses higher than 125 Gy. The STERIN - 300 maintained the word "NOT" in most cases except at doses close to 300 Gy (i.e., 290 Gy) when it completely disappeared.

IAEA Research Contract POR / 8165 / R1 "Establishment of Technological Parameters to Irradiate Dried Fruits for Disinfestation".

Identification of Irradiated Foodstuffs

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[2]*Nuclear and Technological Institute, ITN, Physics, E. N., 2685 Sacavém, Portugal*
[3]*Technical Superior Institute, IST, Av. Rovisco Pais, 1096 Lisboa Codex, Portugal*

During 1997, the case of dried fruits has been studied by EPR using two protocols, the "official EN 1787" protocol for food containing cellulose and the "draft BCR" for food presenting a "sugar-like" signal. The dried fruits studied were: almonds, dates, raisins and pistachio.
After 2-3 months of gamma irradiation the almonds (skin) and pistachio (shell) have presented a "cellulose" signal, the dates (stone) a "complex" signal and the raisins (dried pulp) a "sugar-like" signal. Six months after the irradiation only the pistachio (shell) has presented a "cellulose" signal and the raisins (dried pulp) a "sugar-like" signal.
The electron irradiated dried fruits only the raisins (dried pulp) have presented a "sugar- like" signal 2-3 months and 6 months after irradiation and the pistachio (shell) has presented a

"cellulose" signal 2-3 months after irradiation. The other fruits have not presented any characteristic signal.
The BRUCKER ECS 106 Spectrometer at the Technical Superior Institute (IST) is being used to this work.

EU contract CIPA-CT-94-0134 "Establishment of Eastern Network of Laboratories for Identification of Irradiated Foodstuffs"

Dosimetry for Radiation Sterilisation of Medical Devices

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The principal objective of this contract is to improve the accuracy of radiation dose delivered in industrial irradiation plants.
This will be done through:

i. intercomparisons between industrial facilities and two calibration laboratories: Risø National Laboratory, DK (Risø) and National Physical Laboratory, GB (NPL), and
ii. through the development of protocols describing standard procedures for the calibration of industrial dosimetry systems.

A workshop to analyse the data of the "first intercomparison" was held in October 13-15, 1997 at Riso National Laboratory, Denmark. Report of the work carried out was presented.
Effectiveness of the procedures and protocols will be tested in a "second intercomparison" study.
Those protocols will support the uniform regulation of the sterile medical device industry throughout the European Union, and promote free trade in radiation sterilised medical devices

EU contract SMT4-CT-96-2077 "Dosimetry for Radiation Sterilisation of Medical Devices"

New Bioactives Forms of Ophthalmologic and Dermathologic Products

Maria E. Andrade
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The aim of this contract is to develop new forms of medicinal bioactives drugs - based on the association of actives principles to colloidal systems: liposomes, niosomes, nanoparticles. Sterilisation by gamma radiation of these news forms such as:

i. liposomal systems for ophthalmology and
ii. colloidal systems for dermatology;

corresponds to the use of a new sterilisation process which will confer to the products a high microbiological quality maintaining the stability and the efficiency of the active principles.

PEDIP II, Contract BAT CC 6000 "New Bioactives Forms of Ophthalmologic and Dermathologic Products"

RADIATION TECHNOLOGY UNIT

Current Work

Irradiation Services to Institutions and Companies

M. E. Andrade[1], J. B. Manteigas[1], N. Coelho[2], J. Venâncio [2], A. Góis [2] and V. Damas[2]and L. M. Ferreira[1],
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Irradiation services to institutions and companies such as: radiation sterilisation of medical devices and pharmaceuticals; radiation decontamination of raw materials, herbs, corks, etc., were supplied.

Co-ordination and Technical Supervision of the UTR

M.E. Andrade, L. M. Ferreira and J. B. Manteigas
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The director of the " Radiation Technologies: Process and Products" has served as co-ordinator and technical supervisor of the UTR since the project phase implementation. By the end of December 1997 the direction of the UTR was committed to the ITN Researchers J.B. Manteigas and M.L. Ferreira.

The global objectives of the UTR are to boost radiation processing technologies utilisation at national level, replacing the conventional technologies in general aggressive to the environment and high energetic consuming

Though, gamma radiation technology transfer, assistance industry and institutions, participation in R&D projects and training has been promoted.