Radiation Technologies: Processes and Products

M. Luísa Botelho

Radiation Technologies: Processes and Products is an interdisciplinary group that uses the holistic approach as the key to conceptualize a research or a service. This interdisciplinarity, using Biology, Chemistry and Physics science, allows the study of a subject from various angles and methods unified by a common goal: the validation of methodologies to understand the subject of study, which core is ionising radiation.

The group *modus operandi* permits a constant connection with Industries, Universities and other Research groups applying its expertise in response to requested services, as a collaborator in a research project or in the transmission of knowledge.

The group activities focus on the delineation, development, validation and application of technologies and processes in various fields, such as Environment, Food and Pharmaceutics. As a fundamental part of the validation studies, Risk Analysis is being applied as a process management tool either in production lines of studied products (*e.g.*: food, devices and pharmaceuticals) or in environmental control (*e.g.* hospital rooms, pharmaceutical industries and buildings energetic certification).

In the scope of ITN mission the group is solicited by the authorities or private industries to undertake a consultant role on sterilization and decontamination procedures mainly applying ionising radiation. The group also develops work with the National and International normalization, standardization and certification bodies (IPQ, CEN and ISO).

The Group's main R&D activities are focused at employing ionising radiation technologies to new processes and applications in Agriculture, Food, Pharmaceutical, Wastewater Treatment, Art and other areas. In order to improve our understanding of the Radiation effects in products integrated methodologies composed by Analytical Methods of Biology, Microbiology, Chemistry and Physics are being used. Molecular Biology new trends based on PCR technique are being developed as a diagnostic tool (*e.g.:* potential pathogenic micro-organisms) and as well as fingerprinting methods to assess the biodiversity profile of environmental samples. On-going R&D in environmental virology is being conducted, namely the inactivation response of enteric viruses (*e.g.* norovirus and adenovirus) to ionising radiation for treatment applications (*e.g.* wastewater, food).

FCT running projects, Pulse Radiolysis (PTDC/QUI-QUI/104229/2008) and RADIART (PTDC/HIS-HEC/101756/2008), are focusing in deepen the ionising radiation effects on liquid/solid matrices. Food Irradiation is also a current group research area. Either in the scope of a "chestnut irradiation" collaboration project (CHESTNUTSRAD - QREN nº 13198/2010) with School of Agriculture of IPB; and as part of an IAEA Coordinate Research Project (CRP D6-RC-1163.2) for development of irradiated food for immune-compromised patients.

Training and "know-how" diffusion are one of the main issues of this Group reflecting in the attainment of academic degrees (Graduation, M.Sc. and Ph.D.) and in the dissemination of obtained results in the scientific community (publications, workshops and conferences).

The financial support of the group is based on projects, sponsored by National (*e.g.* FCT, AdI) and International (*e.g.* IAEA) science foundations and expertise services to Industrial Companies.

Researchers
M.L. BOTELHO, Aux., Group Leader
S. CABO VERDE, Aux.
P. SANTOS, Post-Doc, FCT Grant

Students
R. MELO, Ph.D. student, FCT Grant
A. ANTÓNIO, Ph.D. student FCT Grant
T. SILVA, FCT/UNL, Master student
I. NUNES, FCUL Master student
J. MADUREIRA, FCT/UNL, Master student
M. BAÇÃO, FCT/UNL, Master student
N. MESQUITA, Ph.D. student, FCT Grant
M. OLIVEIRA, graduation student from ESAS

Technical Personnel
H. MARCOS

Collaborators
C. CANTO E CASTRO, ITN Network Manager
J.P.LEAL, UCQR., ITN Researcher
P. MATOS, Technical Director of CHIP,S.A
J. TRIGO, INIAP Researcher
P. MAZARELO and S. XISTO, LM Researchers
R. TENREIRO, DBV-FCUL Professor/ICAT
S. J. NASCIMENTO, F.F./ U P, Professor
A. VIEIRA, FCT-UNL, Professor
E. FERNANDES, IST, Professor
J. REIS, Professor, Fac Veterinária, UE

Kinetic study of biorecalcitrant compounds degradation by pulse radiolysis

P.M.P. Santos, A. A. Amílcar[1], R. Melo, S. Cabo Verde, T. Silva, H. Marcos, I. Nunes, J. Madureira, M. Bação, J.P. Leal and M. L. Botelho

Objectives

To use pulse radiolysis technique to study the mechanistic details of the degradation of biorecalcitrant compounds present in industrial (*e.g.* phenolic acids) and municipal discharges (*e.g.* pharmaceuticals), induced by free radicals formed upon radiolysis of aerated water (hydroxyl radical, hydrogen atom, superoxide anion radical and hydrated electron).

Results

Since 2001 the Radiation Technologies: Processes and Products Group has been doing studies on the impact of ionising radiation in the wastewater looking for the advantages and/or disadvantages of the technology application in different kinds of wastewater. These studies covered several fields (*e.g.* chemistry, microbiology and physics). Currently we intended to study the degradation reaction mechanisms of model compounds and predict its radiolysis by-products.

The upgrading of the linear accelerator (LINAC) installed in ITN during 2008 (under FCT Project REEQ/996/BIO/2005) is being performed to work in a pulsed technique. Meanwhile, stationary radiolysis studies with model compounds (*e.g.* gallic acid (GA)) were performed.

Therefore, these integrated studies will be rather useful to assess ionising radiation as a complementary wastewater treatment technology. Concerning the work in progress, several studies have been performed in order to predict a degradation reaction mechanism of GA. This compound is a well known recalcitrant compound present in cork wastewater. Thus, its radiolytic degradation could reduce the high toxicity of these waters.

Standard GA solutions were irradiated in the Co-60 experimental source (Precisa 22) at 1, 9 and 38 kGy at 2 kGy/h. The UV-Vis spectra of non-irradiated and irradiated GA solutions (1 mM) present two absorbance maxima at 269 nm and 212 nm (see Fig. 1).

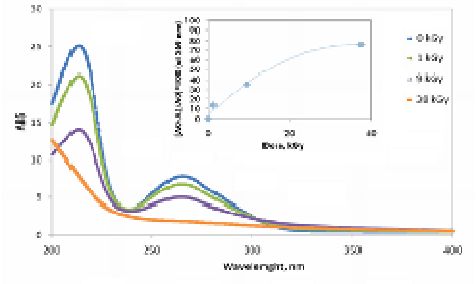

Fig. 1 - UV-Vis spectra of the non-irradiated and irradiated 1 mM GA. Inset: calculated degradation of GA (considering the 269 nm peak) versus irradiation dose.

[1] School of Agriculture, Politechnical Institute of Bragança, IPB, Portugal.

Increasing the radiation dose the absorbance of the peaks overall maximum decrease, which indicate that irradiation effectively degrade GA. The amount of the degradation can be estimated by defining a degradation factor ($(A_0\text{-}A)/A_0\times100$, where A_0 and A are absorbencies of GA solutions at 269 nm prior to and after irradiation, respectively). This factor increase, not linearly, with the dose reaching approximately 76% at 38 kGy (see inset in Fig. 1). However, even at 9 kGy GA degradation reaches almost 35%.

Previous pulse radiolysis studies made in the Department of Chemistry of the Institute of Isotopes (Budapest, Hungary) showed that the hydroxyl radical and hydrogen atom intermediates of water radiolysis react with the solute molecules yielding cyclohexadienyl radicals and generated phenoxyl radicals by loss of water. The GA intermediates formed during reaction with primary water radicals and in the presence of oxygen are transformed to non-aromatic molecules, e.g., to aliphatic carboxylic acids. The Electrospray Ionization Mass Spectrometry (ESI-MS) was used to identify the final by-products of the GA degradation. Based on these results a general reaction sequence for the degradation of GA by gamma radiation is proposed (Fig.2)

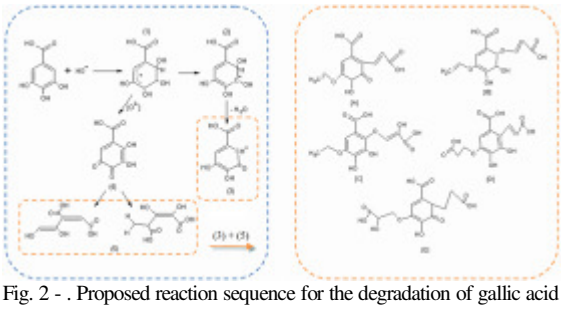

Fig. 2 - . Proposed reaction sequence for the degradation of gallic acid by gamma radiation and some of the possible radiolytic products.

The proposed radiolytic-formed compounds are multi-carboxylic acids and still have the benzenic ring. This proposal is consistent with the fact that the decreasing peak at 212 nm remains present (see Fig. 1) since the smaller radiolytic-formed compounds still have some hydroxyl groups connected to the ring, whereas the one at 269 nm almost disappear (most of the carboxylic groups are broken away from the benzenic ring).

On-going studies focus on the radiolytic degradation mechanisms of other model compounds (*e.g.* acetovanillone and esculetin) by pulse radiolysis.

Published work

Melo, RP; Leal, JP; Botelho, ML. (2011) "Radiolytic degradation mechanism of gallic acid and its end-products" Rapid Communications in mass spectrometry Vol.25 Issue: 1 Pages: 218-222 DOI: 10.1002/rcm.4803.

Application of ionising radiation on the cork wastewater treatment: antioxidant capacity evaluation
J. Madureira, R. Melo, M. L. Botelho

The effects of ionising radiation in cork boiling water are being studied to assess the potential increase of its antioxidant capacity due to hydroxyl radicals' ($OH^{\bullet}$) reactions. Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) were measured to analyze the gamma radiation effects in terms of organic matter content. Total phenolic and antioxidant capacity by Ferric reducing antioxidant power (FRAP) assay were analyzed to predict the effects of this technology in the antioxidant properties. The samples were irradiated at a Co-60 source at several doses (2, 10, 20, 50 kGy) at two different dose rates (0.4 $kGy.h^{-1}$ and 2.4 $kGy.h^{-1}$). The concentration of oxidable organic matter (expressed in terms of COD) decreases, at both dose rates, with increase of absorbed doses. The TOC content do not decrease due to the breaking of organic molecules in other organic molecules of low molecular weight. At 2.4 $kGy.h^{-1}$ the increase of phenolic compounds is higher (29% to 50 kGy) than at 0.4 $kGy.h^{-1}$ (6% to 50 kGy).). This phenomenon could be explained due to that lower dose rate could not be able to destroy the benzenic ring of the tannins and other phenolics, and only break the bonds and rearrange structures, increasing the concentration of smaller phenolic structures. Concerning the FRAP assay, results show an increase of antioxidant activity with irradiation which could be related with the increase of total phenol concentration connected with $OH^{\bullet}$ radical addition. These results associated to the well-known gamma radiation disinfection effect could be an important issue to the development of advanced oxidation processes as a complementary technology on wastewater treatment processes helping its reuse. These studies are under the scope of the IAEA Coordinate Research Project CRP 1539 "Radiation Treatment of Wastewater for Reuse with Particular Focus on Wastewaters Containing Organic Pollutant".

Food Irradiation: raspberries irradiation
S. Cabo Verde, I. Nunes, P. Santos, A. António[1], T. Silva M. J. Trigo[2] M.L. Botelho

Under the scope of the IAEA Coordinate Research Project CRP D6-RC-1163.2 "Development of Irradiated Foods for Immuno-compromised Patients and Other Potential Target Groups" it was intended to evaluate the irradiation effects on fruit and vegetables and the potential extension of shelf-life, in order to improve the safety and variety of immune-compromised patients diet. The nutritional value of raspberry fruit is widely recognized and is demanded by consumers, especially for protection against several diseases, as well as for general health benefits. Based on that, fresh packed raspberries (*Rubus idaeus*) were irradiated at a Co-60 source at several doses (0.5; 1 and 1.5 kGy) at a dose rate of 2.2 kGy/h with a uniformity of dose of 1.23. Microbiological, physico-chemical and sensorial parameters were assessed after irradiation and during storage time. The characterization of raspberries microbiota point out to an average bioburden value of 10^2 cfu/g and to a diverse microbial population predominantly composed by two morphological types [gram-negative, oxidase-negative rods (34%) and filamentous fungi (41%)]. The inactivation studies on the raspberries mesophilic population indicated a one log reduction of microbial load (95% inactivation efficiency for 1.5 kGy). However after irradiation, the surviving population was mainly constituted by filamentous fungi (79 – 98%), being morphologically identified potential pathogenic/opportunistic fungi such as, *Fusarium* sp. and *Alternaria* sp.. Regarding raspberries physico-chemical properties, irradiation caused a decrease in firmness compared with non-irradiated fruit. Nevertheless, non-irradiated and irradiated fruit presented similar physico-chemical and sensory properties during storage time. Based on the microbiological results, the potential application of raspberries in immune-compromised patient's diet could be questionable.

[1] School of Agriculture, Politechnical Institute of Bragança, Portugal;[2] National Institute for Agricultural Research and Fisheries, Portugal.

Irradiation as a potential conservation treatment for art objects
I. Nunes, T. Silva, S. Cabo Verde, M. L. Botelho

Art biodeterioration is one concerning issue that leads to the necessity of developing new approaches in restoration, preservation, conservation and decontamination areas. Studies were performed in order to evaluate the potentiality of gamma rays as a conservation treatment for cultural assets. Namely, the determination of a minimum dose to attain the decontamination and a maximum dose that preserve the studied art objects. Irradiation of ceramic tiles and parchment samples were performed in the Co-60 experimental source (Precisa 22) at a dose rate of 2.2 kGy/h. Sub-lethal doses (1 – 15 kGy) were applied to verify microbial population inactivation profiles on tiles and parchment samples. For tiles, it was observed a significant microbial population decrease of approximately 25% ($P < 0.05$) for irradiation doses higher than 2 kGy. The results also indicated the prevalence of the filamentous fungi (86%) in the surviving population. For parchment samples it was verified microbial inactivation efficiencies higher than 90% for doses > 4 kGy. The higher dose survivors in parchment belong mainly to the groups of Spore forming gram-positive rods and Filamentous fungi. Concerning irradiation effects on tiles physical appearance it was visible an increase in the ceramic opacity and a darkness of blank pigment with radiation dose. However, a maximum gamma radiation dose of 30 kGy suggested no significant modifications in parchment texture and colour characteristics, based on the evaluated parameters and their conditions. Results indicated the potentiality of gamma radiation in a range of 5-10 kGy as effective for parchment documents decontamination treatment.
These studies are under the scope of the projects RADIART (1 BIC) and MYCHOARCHIVE (1 Ph.D.; 1 McS).

Nuclear Instruments and Methods

João B. Manteigas

The strategy of the group involves activities in the following lines:

1. Modelling of radiation fields, calculation of neutron physic parameters, measurement of neutron cross-sections;
2. Modelling and applications of gas discharges;
3. Development of software for control and data analysis;
4. Design of electronic instrumentation for nuclear applications;
5. Instrumentation and technical assistance;
6. Co-operation with other institutions.

Modelling of radiation fields, calculation of neutron physic parameters

Monte Carlo calculations have been carried in the framework of the n_TOF Collaboration (ITN participation on the n_TOF-Ph2 experiment at CERN).

Measurement of neutron cross-sections

The analysis of the data for cross-section measurement, taken in the TOF spectrometer installed at the CERN, was carried out.

Modelling and application of gas discharges

1. The study of methane conversion by a non-thermal plasma produced by a dielectric barrier discharge system (DBD) to obtain Syngas and other hydrocarbons has continued with (a) study of the influence on rectangular voltage pulses on conversion and selectivity, (b) the study of the electron kinetics in methane/carbon dioxide/helium mixtures and, (c) development of theoretical models to explain the variation of i) the breakdown voltage with rare gas concentration and, ii) the conversion fractions with the specific input energy.
2. The study of a dielectric barrier discharge system for processing of polymers by a non-thermal plasma for industrial applications.
3. The construction of a RF-plasma needle with application in biology and medicine.

Development of software for control and data analysis in nuclear spectrometry

The development of free software has continued with the support of EPICS-based gamma spectrometry equipment on the *PyMCA* software for X-ray analysis.

Instrumentation and technical assistance

1. The main objectives are the development of equipment for ITN groups, fabrication of equipment for specific applications and assistance to industrial companies and scientific institutions as well as technical consulting.
2. The technical assistance takes mainly the forms of specialised consultant engineering advice, installation of nuclear gauges, including calibration maintenance and repair and recharging of gauges with imported radioactive sources.
3. The group started providing maintenance and repairing services of HPGe detectors as well as technical advice in the installation of gamma spectrometry equipment.

Co-operation with other institutions

1. Plasma Physics Centre / Gas Electronics Group, IST;
2. ISEL, Dept. of Automation and Electrotechnical Engineering;
3. Comenius Univ., Dept. of Experimental Physics, Bratislava, Slovakia;
4. Leibniz Institute for Plasma Science and Technology, Greifswald, Germany;
5. Research Institute for Solid State Physics and Optics, Budapest, Hungary;
6. n_TOF collaboration, a consortium of several laboratories in Europe, USA and Japan.

Research Team

Researchers

J. MANTEIGAS, Aux., Group Leader
C. CRUZ, Aux. (20%);
I. F. GONÇALVES, Aux.
J. NEVES, Aux.
N. PINHÃO, Aux.

Students

C.M.CARRAPIÇO, Ph.D. Student, IST (IG)
R. SARMENTO, Ph.D. Student, IST (IG)
R.P.F. MENDES, Collaborator (NP, 15%)
A. JANECO, Ph.D. Student (NP)
S. BARROS, Ph.D. Student (IG)

Technical Personnel

T. JESUS
N. INÁCIO
M. CABAÇA

Collaborators

GABRIEL SILVA (10%)

Technical Assistance in the Field of Engineering Applications of Radiation and Radioisotopes

J. Manteigas, J. Neves, N. Pinhão

Objectives

The main objectives are the development of equipment for internal groups, fabrication of equipment for specific applications and assistance to industrial companies and scientific institutions as well as technical consulting.

Results

A summary of the more relevant work carried out is:

(i) Collaboration in corrective and preventive maintenance of the "Ion Beam Laboratory" – TANDEM 3 MV" at the Physics Unit.

(ii) Optimization of the electronic device "Photo-multiplier Divider" for the BaF_2 calorimeter under the project n_TOF-Ph2 experiment at CERN.

(iii) Services in nuclear spectrometry;

(iv) Development and maintenance of electronic equipment to UFA, UPSR, URSN, UCQR and UTR.

Summary of the more relevant Services/Equipment rendered in 2011

Activity	Qty	Client
Electronic Equipment Laboratory equipment for the determination of radioactive element traces by electrodeposition	4	NATS (Qatar)
	1	Dr. Henry Ben (Polónia)
Electronic Equipment Technical Assistance to Nuclear Equipment	21	EMA21 – Portucel/Soporcel (Cacia/Portugal)
	20	EMA21 – Portucel/Soporcel (Cacia/Portugal)
	6	SIDERURGIA NACIONAL (Seixal/Portugal)
	1	ENDRESS+HAUSER (Portugal)
	8	ITN (URSN, UCQR, UPSR) (Portugal)
Prices including TAX (VAT)		**Total Amount: 20 747,66 €**

Participation of ITN in the n_TOF-Ph2 experiment at CERN (5th year)

I. F. Gonçalves, P. Vaz, C. Cruz, J. Neves, C. Carrapiço, R. Sarmento, S. Barros

This project is the continuation of the involvement of ITN in the activities of the n_TOF Collaboration. Since February 2011 the ITN continued the analysis of the data recorded from 2004 till 2010, in collaboration with INFN-Bari and CEA-Saclay, as well as the feasibility studies associated to the construction of the second experimental area. The ITN team participated in several data taken shifts at CERN and is strongly involved in collaboration with Bari and Saclay, in the following areas: Monte Carlo simulation - full and detailed simulation of the geometry of the new experimental area with the usage of Monte Carlo codes MCNPX and GEANT-4; data analysis of the data on neutron capture on U-233 and the analysis of the resonances data on neutron-induced fission on U-236 and Am-241, Am-243 e Cm-245, taken during 2004 using the FIC ("Fast Ionization Chambers") detectors; data analysis of the Fe isotopes (of relevance for innovative technological systems and for Nuclear Astrophysics).

Conversion of methane by a non-thermal plasma using rare-gas/CH_4/O_2 and rare-gas/CH_4/CO_2 mixtures on a dielectric barrier discharge system

J. Branco, N. R. Pinhão, A. Janeco, A. Ferreira, L. Redondo

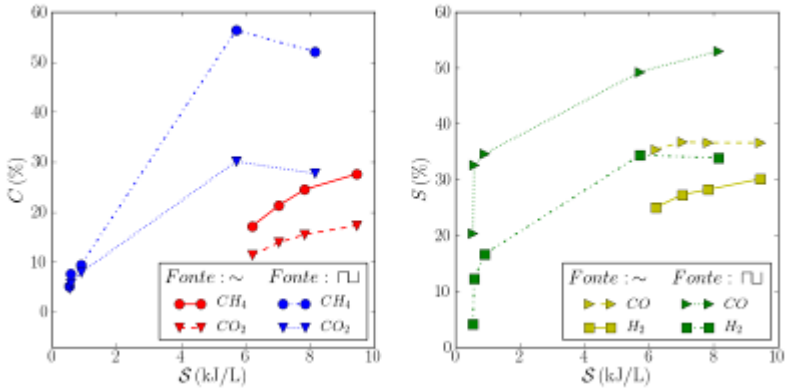

Fig 1- Dependency of conversion, C, for CH_4 and CO_2 and selectivity, S, for CO and H_2 with the specific energy with the voltage pulse shape (sinusoidal or rectangular).

The direct conversion of methane into *Syngas* and other hydrocarbons by a non-thermal plasma is an interesting alternative to the established production process. The study of the conversion of CH_4/CO_2 mixtures in a non-thermal plasma has continued with (i) the study of the influence of the voltage pulse shape of a DBD (dielectric barrier discharge) on conversion and selectivity; (ii) the study of the electron kinetics and, (iii) the development of models for the discharge breakdown. The theoretical model developed is able to explain the results obtained for the breakdown voltage.

Development of software for control and data analysis in nuclear spectrometry

R.P.F. Mendes, N.R. Pinhão

The development of Free Software for gamma and X-ray spectrometry has continued with the extension of the *PyMCA* software (for analysis of X-ray spectra) to support gamma spectrometry and online acquisition from remote equipment based on the EPICS libraries for distributed control of scientific equipment.

***Development of atmospheric non-thermal plasma sources for applications in material and biological* sciences**

N.R. Pinhão, J. Neves

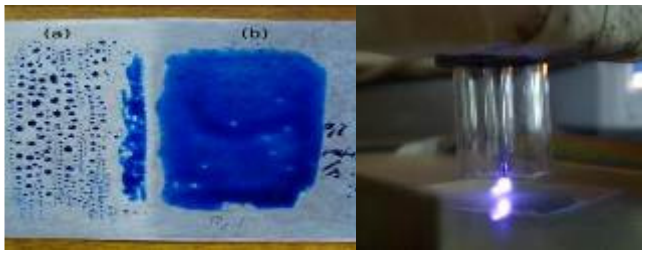

Fig 1 - A - Results on the wettability of a polyvinyl acetate: (a) untreated, (b) treated with a corona discharge. B – Plasma needle discharge at 3 W.

The treatment of surfaces at atmospheric pressure with non-thermal plasmas is an increasingly important field.

The development of two different plasma sources has started: a corona/dielectric barrier discharge system for processing of polymers and a RF-frequency plasma needle for biological and medical applications.