

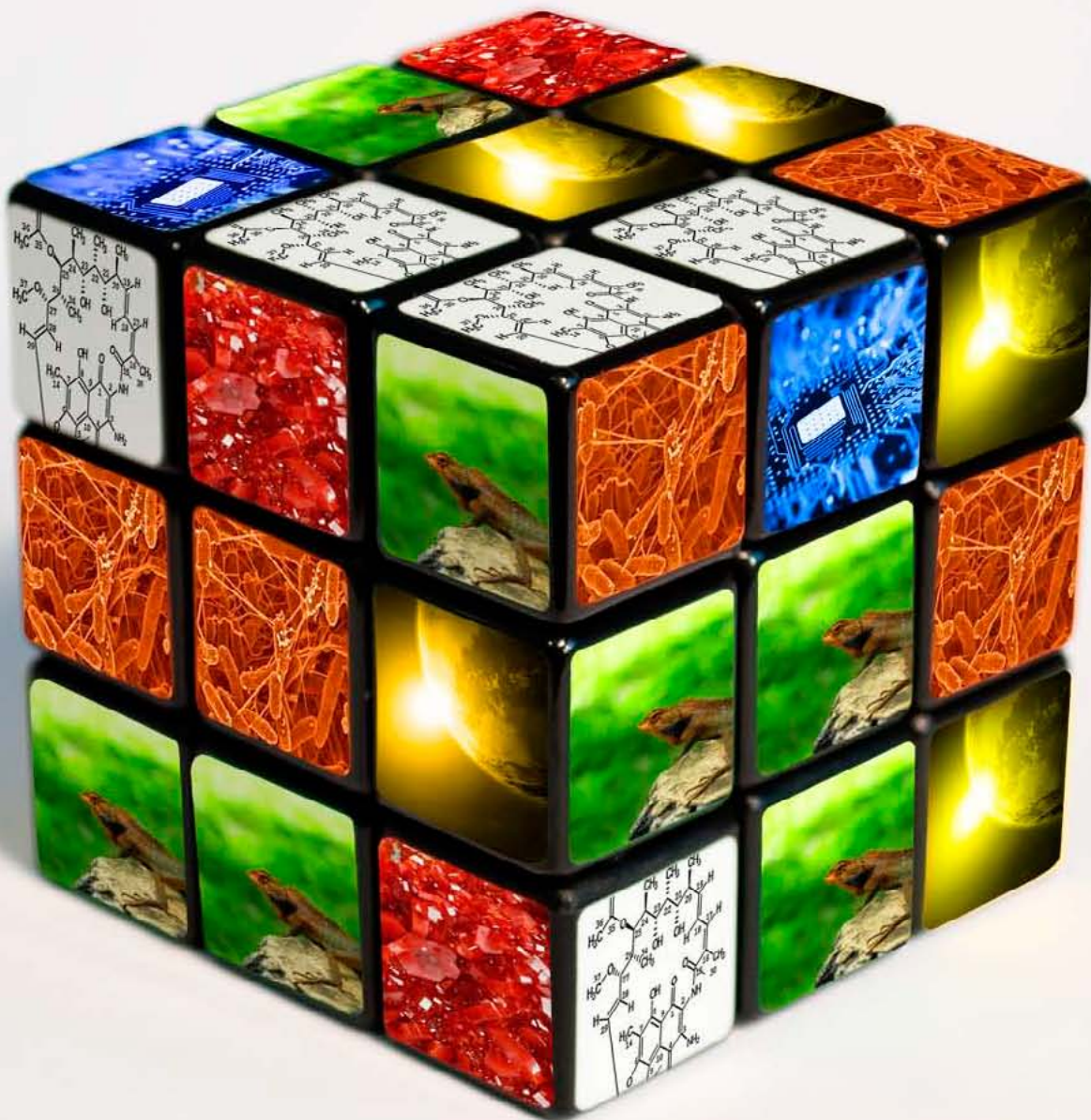
# 2014

Otsailak 12 - 13 de Febrero

## Zientzia eta Teknologia Fakultateko IV. Ikerkuntza Jardunaldiak

### IV Jornadas de Investigación de la Facultad de Ciencia y Tecnología

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Facultad de Ciencia y Tecnología



Euskadi  
2006

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Universidad  
del País Vasco

Euskal Herriko  
Unibertsitatea

## Dekano andrearen gutuna

Adiskideak,

Dakizuen bezala, IV. Ikerkuntza Jardunaldiak otsailaren 12an eta 13an ospatuko dira Zientzia eta Teknologia Fakultatean.

Jardunaldiak asteazkena, otsailak 12an, burutuko dira Paraninfoan. Hasiara ekitaldia goizeko 10:00tan emango da Eusko Jaurlaritzako Zientzia Politikarako Zuzendaria den Miren Begoñe Urrutia eta Ikerkuntzaren Errektoreordea den Fernando Plazaolaren agerpenarekin. Egun berean, 10:15etan Pediatria Katedradun Pablo Sanjurjo Doktorea, Gurutzetako Ospitalean Metabolopatia Unitateko Zuzendaria denak emango du Inaugurazioko hitzaldia. Hitzaldiaren izenburua: “Gaixotasun metaboliko arraroak, zientzia beraren osotasunaren erronka”.

Beranduago, 11:30etatik 12ak arte kafea hartzeko aukera egongo da eta ondoren Fakultateko Grande Sallen posterrak ikusteko bisitaldi gidatua. Azkenik, 12:00ak aldera esleitutako gelatan ahozko aurkezpenak burutuko dira hurrengo arloen inguruan: 1) Biozientziak, 2) Fisika eta Ingeniaritza Elektronikoa, 3) Matematika, 4) Geologia, 5) Kimika eta Ingeniaritza Kimiko

Ostegunean, otsailak 13, 11:30etatik 12:00ak arte Grande Sallen kafea hartzeko parada egongo da eta gero, posterren bisita gidatua. 12:00etatik 13:30ak arte Master eta Doktoretza Ikasketen eskaintzaren aurkezpena egingo da Paraninfoan, Doktoretza eta Master Eskolako Zuzendaria den Gabriela Chotro eta Master eta Doktoretza programen arduradunen partaidetzarekin.

Ikus dezakezuen bezala, interes handiko jardunaldiak dira Ikasleentzako. Horregatik, ikasleak aurrez aipatutako ekintzen agerpenarekin partaidetza bultzatzea eskatzen dizuegu.

Adeitasunez,

Esther Domínguez  
Zientzia eta Teknologia Fakultateko Dekano Andrea

## Carta de la Decana

Estimados compañeros y compañeras,

Como ya sabéis, durante los días 12 y 13 de febrero se celebrarán las IV Jornadas de Investigación de la Facultad de Ciencia y Tecnología.

El miércoles día 12 a las 10.00 h tendrá lugar en el Paraninfo, la Inauguración de las Jornadas con la presencia de la Directora de Política Científica del Gobierno Vasco, Miren Begoñe Urrutia y del Vicerrector de Investigación, Fernando Plazaola. Seguidamente, a las 10.15 tendrá lugar la Conferencia Inaugural a cargo del Dr. Pablo Sanjurjo, Catedrático de Pediatría, Director de la Unidad de Metabolopatías del Hospital de Cruces, titulada “Enfermedades Raras Metabólicas : un reto para la ciencia en su conjunto”.

A continuación de 11.30 a 12.00 habrá un café y se procederá a una visita guiada a los pósteres, en la Grande Salle de la Facultad. Seguidamente, a las 12:00 se presentarán, en las salas asignadas, las comunicaciones orales de forma simultánea para las distintas áreas: 1) Biociencias; 2) Física e Ingeniería Electrónica; 3) Matemáticas; 4) Geología y 5) Química e Ingeniería Química.

El jueves día 13 de 11.00 a 12.00, café en la Grande Salle y visita guiada a los pósteres. A continuación de 12.00 a 13.30 en el Paraninfo tendrá lugar la Presentación de la Oferta de Estudios de Máster y Doctorado de la Facultad, con la participación de Gabriela Chotro, Directora de la Escuela de Máster y Doctorado y Responsables de los Programas de Master y Doctorado.

Dado que estas Jornadas son de gran interés para el alumnado, os pedimos que impulséis su participación, trasladando la presencialidad del aula a las actividades programadas.

Recibid un cordial saludo,

Esther Domínguez  
Decana de la Facultad de Ciencia y Tecnología

Dear colleagues:

As you know, the 12th and 13th February we will hold the Fourth Conference on Research of the Faculty of Science and Technology.

Wednesday 12th at 10.00 in the auditorium the inauguration of the conference will take place, attended by the Director of Science Policy of the Basque Government, Miren Begone Urrutia and Vice Rector for Research, Fernando Plazaola. That same day at 10.15 is the Inaugural Lecture by Dr. Pablo Sanjurjo, Professor of Pediatrics, Director of Metabolic Disorders Unit of the Hospital de Cruces, entitled "Rare Metabolic Diseases : a challenge for science as a whole".

Then from 11.30 to 12.00 there will be coffee and we'll proceed to a guided tour of the posters in the Grande Salle of the Faculty. Finally, at 12.00 in the assigned rooms, the presentations will take place simultaneously for different areas: 1) Biosciences 2) Physics and Electronic Engineering 3) Mathematics 4) Geology and 5) Chemical and Engineering Chemistry .

Thursday 13 from 11.00 to 12.00, coffee in the Grande Salle and guided tour of the posters. Afterwards, from 12.00 to 13.30 in the auditorium we'll have the presentation of the offer of Masters and Doctoral School, with the participation of Gabriela Chotro, Director of the Masters and Doctoral School and the persons in charge of the Programmes for Masters and Doctorates.

As you can see, these conferences are of great interest to students.

Therefore, we ask you to promote participation, transferring classroom presence to the activities scheduled.

Best regards,

Esther Domínguez  
The dean of the Faculty of Science and Technology

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Ahozko komunikazioak

**ABSTRACTS**

Comunicaciones orales

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# Biozientziak: Alderdi Molekularrak



Biociencias:  
Aspectos moleculares

# Comparative membrane proteomic analysis between *Staphylococcus epidermidis* CECT 231 grown in biofilm or planktonic conditions

Águila-Arcos, S.<sup>1,2</sup>, Ding, S.<sup>3</sup>, Carroll, J.<sup>3</sup>, Aloria, K.<sup>4</sup>, Arizmendi, J.M.<sup>1,4</sup>, Fearnley, I.M.<sup>3</sup>, Walker, J.E.<sup>3</sup>, Goñi, F.M.<sup>1,2</sup> and Alkorta, I.<sup>1,2</sup>

<sup>1</sup>Department of Biochemistry and Molecular Biology, University of the Basque Country, UPV/EHU, Leioa, Spain; <sup>2</sup>Unidad de Biofísica (CSIC, UPV/EHU), Leioa, Spain; <sup>3</sup>The Medical Research Council Mitochondrial Biology Unit, Cambridge, UK; <sup>4</sup>Proteomics Core Facility-SGIKER ProteoRed, University of the Basque Country, UPV/EHU, Leioa, Spain

KEY WORDS: biofilms, membrane proteome, drug target.

*Staphylococcus epidermidis* has emerged as one of the major nosocomial pathogens associated with infections of implanted medical devices. The most important factor in the pathogenesis of these infections is the formation of bacterial biofilms. Bacteria grown in biofilms are more resistant to antibiotics and to the immune defense system than planktonic bacteria and antimicrobial therapy may fail unless the biofilm-coated implanted device is removed. Therefore the development of new therapeutic approaches based on the search for new bacterial drug targets is required. In this regard, the comparative membrane proteome analysis of *S. epidermidis* CECT 231 grown under biofilm and planktonic conditions will contribute to identify proteins involved in biofilm formation as therapeutic targets.

In this study three proteomic approaches were performed to investigate membrane proteins associated to biofilm formation: i) sample fractionation by gel electrophoresis, followed by isotopic labelling and LC-MS/MS analysis, ii) in-solution sample preparation, followed by isotopic labelling and LC-MS/MS analysis, and iii) in-solution sample preparation and label-free LC-MS/MS analysis. Differences in the membrane proteome were observed between the two different growth conditions, showing higher levels of five proteins associated with pathogenesis in biofilms: accumulation associated protein, staphylococcal secretory antigen, signal transduction protein TRAP, ribonuclease Y and phenol soluble modulín beta 1.

The polysaccharide intercellular adhesin (PIA) encoded by the *ica* operon is one of the major factors involved in biofilm formation. However, *ica*-negative staphylococcal strains are able to form biofilms and proteins such as the accumulation associated protein (Aap) take an important role in this biofilm formation process. In this work we demonstrated that the *ica*-negative strain *S. epidermidis* CECT 231 showed a higher expression of Aap under biofilm growth conditions than under planktonic growth conditions.

According to these results we can conclude that *S. epidermidis* CECT 231 expresses different proteins under biofilm and planktonic growth conditions, showing a higher abundance of virulence proteins under biofilm growth conditions. Additionally the accumulation associated protein (Aap) seems to be involved in the biofilm formation process. Consequently, this protein may be a good therapeutic target.

# Understanding disorders of the visual system and promoting repair and regeneration

## Neuro-ophthalmo Biology Group

Elena Vecino<sup>1</sup>, Jennifer R. Higginson<sup>1</sup>, Noelia Ruzafa<sup>1</sup>, David Rodríguez Fernández<sup>1</sup>, Juan Durán de la Colina<sup>2</sup>, Javier Araiz<sup>2</sup>, Javier Haritz Urkola<sup>3</sup>, Alex Fonollosa<sup>4</sup>, Marta Galdós<sup>4</sup>, Sergio Pinar<sup>4</sup>

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KEY WORDS: retina, cornea, glaucoma, uveitis, neuroprotection, retinal ganglion cells, glia, computational, ocular surface, primary cell cultures.

We are a multidisciplinary group consisting of ophthalmologists, biologists, biochemists, physicists and veterinarians and currently have 15 members. We have been working together for the last 18 years. Our group has been recognised by the Basque Government and they awarded us with 6 years of funding from 2010-2015. Our lab is located in the Faculty of Medicine in the Department of Cell Biology and Histology but members of the group also work in Hospitals such as Cruces, San Eloy, Donostia and Txagorritxu. The director of the group GOBE (Grupo de Oftalmo-Biología Experimental) [www.ehu.es/GOBE](http://www.ehu.es/GOBE) is Prof. Elena Vecino from the Faculty of Science and Technology.

Within GOBE there are four main areas of research:

1. **Neuroprotection** of retinal ganglion cells by retinal glia (PI: Prof. Elena Vecino). Understanding the molecular mechanisms that lead to the death of retinal ganglion cells (RGCs) in retinopathies such as **glaucoma**. RGCs are neurons that transport visual signals from the retina to the brain and their loss, after disease or injury, leads to irreversible blindness. By studying the molecular interactions between RGCs and glia, which are the supportive cells of the retina, we hope to understand how we can prevent cell death and instead promote RGC regeneration. In this project we collaborate with researchers at the University of Salamanca, Cambridge University and New York Medical College. The **computational** non-invasive characterisation of cellular changes within the normal and pathological retina is an aspect that the group is interested in and we are currently collaborating with physicists from UPV/EHU and Bordeaux University.
2. **Ocular surface** regeneration (PI: Prof. Juan Durán). Focussed on researching factors present in the tears, that can promote the repair of the injured ocular surface, in particular the corneal epithelium. In this project we have been collaborating with a proteomics expert, Prof. JM Arizmendi at the FCYT.
3. **Analysis of aqueous humor in glaucoma** patients (PI: Dr Javier Haritz Urkola). Analysing the viscosity of aqueous humor in patients with glaucoma to detect any changes compared with healthy patients. Aqueous humor is a transparent, gelatinous fluid that is secreted from the ciliary epithelium and is located in the space between the lens and the cornea. Alterations in its composition may help us understand more about how glaucoma progresses.
4. **Uveitis** (PI: Dr. Alex Fonollosa) Uveitis is a general term describing a group of inflammatory diseases that produces swelling and destroys eye tissues. Dr Alex Fonollosa's group are interested in understanding more about uveitis and are currently studying retinal cell cultures to test the possible action of somatostatin in the tight junctions formed in the retina-pigment epithelium. These basic studies are done in collaboration with SGIker and biotech companies with the aim of developing clinical applications.

Together we have a shared interest in studying disorders of the visual system using different approaches. A total of 10 PhD theses have been supervised by members of GOBE in the last 10 years and 7 more are being carried out at present, as well as several Masters and Graduate theses.

**Investigative Techniques** used in our research are: immunohistochemistry, electron microscopy analysis, primary cell cultures of retinal cells, organ-explant cultures, eye microsurgery, animal models (ischemia and glaucoma), computer vision.

# Ceramide 1-phosphate stimulates cell migration and invasion in pancreatic cancer cells.

---

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KEY WORDS: cancer, ceramides, pancreas.

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Pancreatic cancer is an aggressive and devastating disease, which is characterized by invasiveness, rapid progression and profound resistance to treatment. Despite recent advances in surgical and medical therapy, little progress has been made to decrease the mortality rate of pancreatic cancer. It is now well established that sphingolipids are important signaling molecules in diverse cellular processes. Simple sphingolipids including ceramides, sphingosine or their phosphorylated forms sphingosine 1-phosphate (S1P) and ceramide 1-phosphate (C1P) have been involved in the control of cell homeostasis, as well as tumorigenesis. In this connection, increasing experimental evidence indicates that modulation of sphingolipid metabolism can reduce cancer cell viability, decrease tumor size, and sensitize cancer to conventional treatments. For many years, our group has focused on the role of C1P in the regulation of cell growth and survival and more recently we discovered that C1P promotes cell migration. In this work, we demonstrate that C1P enhances cell migration and invasion in the human pancreatic cancer cell line PANC-1. C1P-stimulated cell migration and invasion were blocked by selective inhibitors of phosphatidylinositol 3-kinase (PI3K) or Akt, also known as protein kinase B (PKB), and by specific siRNAs to silence the genes encoding for these kinases. We also found that the MAPK pathway and the small GTPase RhoA, which has been described to control cytoskeleton reorganization, are involved in C1P-stimulated cell migration and invasion. Our recent studies indicate that C1P-stimulated cell migration can be also inhibited by pertussis toxin (Ptx), a potent inhibitor of Gi proteins, thereby suggesting that C1P induces cell migration / invasion through interaction with a specific Gi protein-coupled receptor.

# Genomics and Health. Application of genomic tools in human and animal diseases.

---

Koldo Garcia-Etxebarria<sup>1</sup>, Amaia Larruskain<sup>1</sup>, Maialen Sistiaga<sup>1</sup>, Itxazne García-Ceciaga<sup>1,2</sup>, Aitor Esparza<sup>1</sup>,  
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<sup>1</sup>Genetics, Physical Anthropology and Animal Physiology Dpt.; <sup>2</sup>Physiology Dpt. UPV/EHU

---

Genomics, Association analysis, obesity, infectious diseases, endogenous retroviruses, host-parasite interactions

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In the *Genomics and Health* group the role of different genomic elements, both genes and “junk DNA”, is studied in different diseases by means of various genetic and genomic methods and tools. In this talk the biocomputational analyses made are summarized.

Regarding **human health**, a multidisciplinary approach, including information on nutrition, biochemical blood parameters and genetic polymorphisms in candidate genes, is being applied to study the obesity inducing factors in a work-environment.

In the preliminary genetic analysis, 32 SNPs (single nucleotide polymorphisms) located in 14 candidate genes which were selected from Whole Genome association analyses were genotyped in a case-control study. Some weak association signals were found, which should be confirmed in the second phase of the study.

As for **animal health**, we are interested in the analysis of host-parasite interactions at the genome level. Instead of a candidate gene approach, we are using a “Genome-wide association analysis” methodology to understand the genetic basic of an ovine viral disease called Visna/Maedi. 50.000 ovine SNPs were analyzed in two sheep breeds. In this study some SNPs were significantly more frequent in cases than in controls. We are currently analyzing the expression of the genes involved in these associations.

Nevertheless, the genes are not the only interesting components of the genome. We detect and characterize transposable elements to assess their importance in the genome structure and in the disease development. Transposable elements are genomic components that are able to translocate within the genome and, in the cases of endogenous retroviruses (ERVs), between genomes as well. The sheep is a convenient model of host-pathogen coevolution due to the interactions of an exogenous retrovirus called JSRV and its endogenous counterparts, enJSRVs. In our group new enJSRVs have been described and their full characterization is being carried out.

Lastly, we have extended the analysis of ERVs to other ruminant species. The transposable elements of the goat were analyzed using new bioinformatic tools. On the whole the number and coverage of different types of transposable elements in goat were similar to those detected in cattle. Most of the bovine ERV families, that is, group of ERVs with the same origin, were common to many other ruminant species also.

# Synthesis of magnetic biocatalysts and its uses to obtain bioproducts

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KEY WORDS: enzyme, biocatalysis, magnetic nanoparticles (MNPs), cross-linked enzyme aggregates (CLEAs), chiral hydroxyalkanoic acids, biodiesel, biosurfactants, oligoesters, bioplastics

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The use of immobilized enzymes in industrial applications often presents advantages over their soluble counterparts, mainly in view of stability, reusability and simpler operational processing. Because of their singular properties, such as biocompatibility, large and modifiable surface and easy recovery, iron oxide magnetic nanoparticles (MNPs) are attractive super-paramagnetic materials that serve as a support for enzyme immobilization and facilitate separations by applying an external magnetic field.

Cross-linked enzyme aggregates (CLEAs) have several benefits in the context of industrial applications since they can be cheaply and easily prepared from unpurified enzyme extracts and show improved storage and operational stability against denaturation by heat and organic solvents. In this work, by using the aforementioned advantages of MNPs of magnetite and CLEAs, we prepared two robust magnetically-separable types of nanobiocatalysts by binding either soluble enzymes onto the surface of MNPs functionalized with amino groups or by cross-linking aggregates of enzymes among them and to MNPs to obtain magnetic CLEAs (mCLEAs). For this purpose the lipase B of *Candida antarctica* (CALB) and the medium chain length-polyhydroxyalkanoate (mcl-PHA) depolymerase of *Streptosporangium roseum* DSM 43021 were used. The hydrolytic and biosynthetic activities of the resulting magnetic nanobiocatalysts were assessed in aqueous and organic media and compared between them and to those showed by the corresponding soluble enzyme.

Thus, the hydrolysis of triglycerides or the transesterification reactions to synthesize biodiesel, biosurfactants or bioplastics were studied using magnetic CLEAs of CALB. On the other hand, the magnetic mcl-PHA depolymerase preparations were used to obtain chiral monomers of (*R*)-3-hydroxyoctanoic acid or furane-derived oligoesters of interest in fine chemical, pharmaceutical and biomedical industries.

This research was funded by grants from UPV/EHU (GIU11/25), the Basque Government (SAIOTEK S-PE12 UN041), MINECO (CTQ2011-25052) and the European Union (POCTEFA EFA217/11, Project ENERGREEN).



# Production of recombinant proteins of *Candida albicans* with proinflammatory and protumoral activity

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KEY WORDS: *Candida albicans*, Immunocompromised, Cancer, Mannoproteins, Alcohol dehydrogenase.

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*Candida albicans* is a dimorphic fungus that can grow in both yeast and filamentous forms. Although it is part of the normal microbial flora, when the patient is immunocompromised, it can disseminate through the blood causing an invasive candidiasis. Once in the blood, the liver is the main organ responsible for the clearance of the infection. In this organ, the yeast adheres to endothelial cells of blood vessels, leading to an inflammatory process. This process, through cytokines and adhesion molecules, recruits immune cells into the site in order to clear the infection. However, when the patient is immunocompromised, as in cancer patients that receive chemotherapeutic treatments, these immune cells may be missing. Hence, when the inflammatory response is activated by the presence of this infectious microorganism, it may occur that tumour cells present in the blood, instead of immune cells, adhere to the liver endothelium. This may become into the first step of a metastatic focus in the liver. Using an *in vitro* model, we have proved that, when endothelial cells are coincubated with *C. albicans*, the adhesion of tumour cells to the endothelium is increased. Lately, we have studied the molecules implicated in this process and identified several mannoproteins of *C. albicans* that increase the tumour cell adhesion the most. This project is focused on the study of proinflammatory and protumoral effect of these characterised mannoproteins.

To obtain these proteins individually, we have cloned five proteins into *Escherichia coli* in order to express the desired recombinant protein. So far, the effect of these proteins on the tumour cell adhesion to the endothelium has been tested. All of them showed capacity to stimulate endothelial cells and consequently increased cancer cell adhesion to endothelium. Among the proteins assessed, alcohol dehydrogenase 1 (ADH1) is the one that induced the highest increase in the adhesion. This protein is also interesting as it produces acetaldehyde, an important carcinogenic compound. The next step is to produce this protein in a *Pichia pastoris* model; because this organism is also a yeast, and therefore, the obtained recombinant protein will be more similar to the one produced by *C. albicans*.

After the production and purification of the protein, we will use ADH1 to stimulate endothelial cells in order to study its effect on the adhesion level of tumour cells to these cells, as done before. Moreover, the level of proinflammatory cytokines in the medium will be measured. In the same way, we will also use a *C. albicans* ADH1 null mutant in order to test the effect of the absence of this protein in the stimulation of endothelial cells by *Candida*. On the other hand, we will also study the effect of ADH1 and the yeast directly in two tumour cell lines (B16 and H357). This effect will be tested by looking at cancer cell viability and proliferation, phagocytosis of the cancer cells over the yeast, and progression of cancer cells into a malignant phenotype, in order to know if this pathogen activates tumour cells and by which mechanisms.

# Análisis proteogenómico de los factores de patogenicidad de *Scedosporium prolificans*

## Proteogenomic analysis of the *Scedosporium prolificans* pathogenic factors

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KEY WORDS: Proteomics, immunomics, antifungal resistance, host-pathogen interactions.

The emerging pathogen *Scedosporium prolificans* has been related to serious, often fatal, infections that cannot be successfully treated with conventional antifungal drugs due to the multiresistance of the fungus. In spite of that *Scedosporium* spp. are widely distributed in humanized media, especially in Spain and Australia, their infections affect, above all, to immunocompromised individuals. Hence, the competent immune system of healthy population seems to play an important role to avoid these infections. Due to the increasing importance of *S. prolificans* in clinics, we are interested in analyzing its pathogenic factors, about which little is known. By applying omic technologies we study different sides of *S. prolificans* pathogenesis:

### Proteomic patterns of *S. prolificans*.

We optimized growth conditions of *S. prolificans* and a workflow for protein extraction, both from conidiospores and hyphae, as proteomics-based techniques have never been applied to study this fungus. By using this optimized working protocol, we performed the first proteomic profiles of the both morphs, conidiospore and hypha, finding more than 350 protein spots were detected by 2-DE in hyphae profiles, while only 250 in conidia.

### Identification of antifungal resistance-related proteins

As mentioned before, *S. prolificans* presents an inherent antifungal multiresistance. This characteristic makes it difficult to successfully treat infections caused by this fungus. However, in-depth analysis of the molecular basis of this resistance could be key in the development of new drugs or therapeutic strategies. Hence, we are analyzing proteomic, morphological and structural changes in the presence of the most efficient antifungal, voriconazole.

### Immunomics against human IgA and IgG

Human humoral response against this fungus is also interesting for us. Hence, we use human samples of saliva and serum in order to study the immunogenic response against IgA and IgG, respectively. We apply 2D-western blot, coupled with mass spectrometry, to identify antigenic proteins which recognition may be essential to the host immune system to kill the fungus, or hamper its growth or adhesion to tissues. Identifying these proteins may be critical as they could be used as targets for passive immunotherapy.

### Analysis of host innate immune response

Immune cell populations, such as macrophages, play key roles during fungal infections. However, few studies have been carried out concerning immune response against *S. prolificans*. Therefore, we will use the cell line ANA-1 (murine macrophages) to study their responses such as production of cytokines, reactive oxygen species (ROS), etc.. Moreover, *Scedosporium* spp. have been described as neurotropic when they disseminate inside the host, so we are also interested in analyzing these parameters by using the microglial cell line BV2 and whole brain organotypic cultures.

These findings may be interesting to progress on the development of innovative antifungal treatments and diagnostic tools that allow improving the strategies against these infections.

# Transcriptomic study of *Aspergillus fumigatus* in different environmental conditions and into the host-pathogen relation

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KEY WORDS: *Aspergillus fumigatus*, microarray, pathogenesis

*Aspergillus fumigatus* is considered the principal airborne fungal pathogen, producing high mortality rate in immunodeficient patients. In this kind of patients the fungal is able to avoid the weak macrophage response and finally penetrates the alveolar epithelial and germinate creating invasive hyphae that are able to disseminate through the bloodstream causing fungal disseminated diseases, named invasive aspergilosis (IA). Traditionally the investigation of the virulence factors of *A. fumigatus* has used knock out strains to detect an attenuate virulence. Actually the evidence of a multifactorial pathogenesis have changed the point of view of the research and now the transcriptomic and proteomic analysis could be the most effective way to study the virulence of *A. fumigatus*. The transcriptomic analysis using expression microarray is one of the best techniques because it allows to study the expression of each gen in different conditions. For this reason the group designed a new customized microarray that covers the entire genome of *A. fumigatus* to improve the understanding of the pathogenesis. The microarray was produced using the information available from the NCBI database and the system e-Array of Agilent Technologies (Santa Clara, CA, USA). This microarray includes 9,630 genes of *A. fumigatus*, 62 quality control genes and positive and negative controls included automatically by the design system.

The aim of the study is the transcriptomic analysis of *A.fumigatus* using our microarray. We have carried out experiments under different environmental conditions. The transcriptome analyzed after the growth of the fungus at 24°C demonstrated that there are a total of 4.874 genes expressed in this condition. The genes involved in pathogenesis expressed at this temperature were 21 genes encoding extracellular enzymes, 1 gene involved in the biosynthesis of a gliotoxin, 5 genes related to iron metabolism and 11 allergenic genes. Furthermore, ten of the genes that there were more expressed, were used to validate the microarray using retrotranscription-qPCR. *A.fumigatus* growth at 37°C showed that there are 4.265 genes expressed in this condition. Between them, 1.253 genes were differentially expressed at 24 or 37°C, but still haven't finished the analysis of virulence-related genes in these conditions. Furthermore, after a preliminary infection study using *A. fumigatus* in co-exposure with macrophages, we will use the technique to study the transcriptome of the fungus when it is exposed to cells, to understand better the host-pathogen relation. Cell research involves working under specific conditions, as presence of fetal bovine serum and culture conditions. These different conditions can also affect the behavior of the fungus, therefore is necessary analyzing the transcriptome in this situation. At last, highlight that we will use several cell lines, as murine macrophages ANA-1 and human alveolar epithelium 16HBE14o, to study the pathogenesis of *A.fumigatus*. Finally we will try to define new therapeutic and diagnostic targets.

# Biozientziak: Ingurune alderdiak



# Biociencias: Aspectos ambientales

# Assessing nanoparticle toxicity using zebrafish (*Danio rerio*) as model organism

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KEY WORDS: metal nanoparticles, acute and sublethal toxicity, zebrafish *Danio rerio*

Human capacity to manufacture materials at the nanoscale is resulting in a new industrial revolution. Applications based on metal nanoparticles (NPs) are an extensively growing field of nanotechnology and NPs are being incorporated in a variety of consumer products. Therefore, especial attention must be paid to the potential effects that NPs released into the environment could produce on ecosystems health. With the aim of studying these potential adverse effects, a set of metal-bearing NPs (CuO, ZnO, TiO<sub>2</sub>, SiO<sub>2</sub>, Ag, Au and CdS) were selected and a two-tier approach was applied using zebrafish (*Danio rerio*) as model organism. In the first-tier approach, newly fertilized zebrafish embryos were exposed following a standardized fish embryo toxicity test to five different concentrations of each type of NP during 120 hours in order to rank NP toxicity. For this purpose, different endpoints were studied: survival rate, hatching rate and hatching time, and malformation prevalence. NP toxicity was studied in comparison with the toxicity exerted by their ionic and bulk counterparts, as well as with that exerted by the additives present in the suspension. Overall, the ionic forms were the most toxic compounds, followed by the NP forms and, finally, the bulk forms. A ranking of toxicity depending on the chemical composition was established, being Ag NPs the most toxic ones, followed by ZnO, CdS, Au, CuO, and finally TiO<sub>2</sub>, SiO<sub>2</sub> and commercial ZnO. A size-dependent effect was observed with some NPs, such as Ag NPs, being the smallest NPs the most toxic to zebrafish embryos. The additives present in some of the suspensions, as acids and surfactants, were partially responsible for the toxicity. Malformations observed after 120 hours of exposure were, among others, yolk sac edema, cardiac malformation, head malformations, spinal cord flexure and fin fold abnormality. Zebrafish embryos were also exposed to fluorescent SiO<sub>2</sub> NPs in order to study uptake and internalization of NPs. During the first 48-72 hours NPs were observed only attached to the chorion surface. After hatching, fluorescent NPs were observed attached to the surface of the fish body, under the gill opercle covering the surface of the gill lamellae, in the gut tract and in the cloacal chamber of the posterior intestine. For the second tier, CuO, Ag and CdS NPs were selected. Adult zebrafish were exposed for 21 days to 0.01 mg metal/L of these NPs and to the same concentrations of the ionic form and then, maintained in clean water up to six months in order to study long-term effects. At this exposure concentration, only cadmium in both forms caused mortality but, according to the lysosomal membrane stability test, all assayed metals significantly impaired general health status of fish. Metal accumulation in exposed zebrafish was detected by chemical analyses, as well as, by autometallography which revealed the presence of black silver deposits in intestine and liver. Histopathological alterations such as aneurism, extensive oedema of epithelial cells and fusion of secondary lamellae were observed in gills. Alterations of liver transcriptome were recorded after 3 and 21 days of exposure to all compounds in both forms. Exposure to ionic cadmium caused the highest number of significantly regulated genes after Limma analysis (adjusted p-value <0.05, Benjamini-Hochberg FDR). Moreover, different groups of genes were regulated exclusively after exposure to each NP, indicating a specific effect associated to the nano form of the metal. In conclusion, some of the NPs currently incorporated in consumer products produce deleterious effects in fish, reducing embryo viability and causing sublethal effects from the molecular to the physiological levels. Therefore, the use of nanotechnologies and nanomaterials offers great possibilities for industrial processes and advanced products but it is necessary to assure the safe use of these materials for both human and environmental health.

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# Traceability of changes in biomarkers depending upon sampling conditions

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KEY WORDS: sampling strategy, biomonitoring, biomarkers, *Mytilus galloprovincialis*.

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In order to harmonize assessment and monitoring procedures for implementing the European Marine Strategy Framework Directive (MSFD) in the Bay of Biscay, one of the main objective of the project entitled “Towards science-based standard biomarker methods, suitable to diagnose and monitor pollution biological effects in the Bay of Biscay for the purpose of implementing the European Marine Strategy Framework Directive”(MINECO 2013-2015) is to optimize existing biomarker methods for mussels by reducing variability and improving sampling, processing and analytical procedures. With this aim, and knowing that there are differences on the collection and pre-processing strategies of mussels between different research teams working on assessment and monitoring programmes, and in order to advance in the understanding of biomarkers variability and responsiveness depending upon sampling strategies, the present study was carried out. Mussels *Mytilus galloprovincialis* were collected from Gorniz, a reference locality of the Basque Coast, in September 2010. Low and high intertidal mussels were handpicked and they were pre-processed differently: *in situ*; transported in air to the laboratory and sacrificed 3 hours after sampling; transported and maintained in water and sacrificed 3 and 24 hour after sampling. Accordingly, a battery of biochemical (glutathione S-transferase (GST); catalase (CAT), glutathione peroxidase (GPx), glutathione reductase (GR); levels of lipids peroxides (LPO); and cholinesterase (ChE)) and cell-level (labilization period of lysosomal membrane (LP); lysosomal enlargement (VvL) biomarkers was measured. Biochemical biomarkers showed higher ChE, GST and GR activities and lower LPO and GPx activities when mussels were pre-processed *in situ*. Although no significant, differences were recorded on lysosomal biomarkers among sampling strategies, LP values trends to be lower and VvL values trends to be higher in mussels pre-processed *in situ*. Overall, the obtained results demonstrate that the sampling strategies could influence on biomarkers. But we must be conscious that we are assessing the environmental health by taking into account a particular moment. Thus, it is concluded that sampling protocols are needed in order to avoid as much as possible natural variability on biomarkers and differences produce in the manipulation of samples.

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# Pigments and fluorescence in the study of extreme environmental conditions

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KEY WORDS: Ageing, antioxidants, ecophysiology, fluorescence, pigments, pollution, proteins, winter photoinhibition.

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## EKOFISKO GROUP

Ekofisko group belongs to Department of Plant Biology and Ecology, more specifically to Plant Physiology Laboratory. The group encompasses two main branches of knowledge: the study of contamination through the use of plants and the ecophysiology of stress in plants. Nowadays, these two lines are focused on different issues: monitoring of pollution in plants and the restoration of polluted soils are the main objectives of the first branch, while, the current lines of research of the second line is the study of the protective responses of photosynthetic organisms living in extreme environments such as the alpine ecosystems. Among these responses, the accumulation of certain pigments (carotenoids) and antioxidants (tocopherols) play a key role in plant acclimation, but also in human nutrition. Thereby the presence of these compounds is also studied in edible plants with the aim to enhance its nutritional value.

Specific techniques used by the Ekofisko group are the analytical determination through HPLC (high pressure liquid chromatography) of compounds involved in protection, such as pigments and tocopherols; the study thylakoidal proteins using Western Blot; the study of photosynthesis through chlorophyll fluorescence measurements with portable fluorometer or imaging fluorometers; acid digestion of soil and plants to metals content determination. The group maintains an intense collaboration with research groups of Spain, Austria, Estonia, United Kingdom, France, Germany, Finland, Australia and Chile.

## IS AGEING IMPORTANT UNDER WINTER STRESS CONDITIONS?

During winter, the combination of low temperatures and high light induces a process known as winter photoinhibition, in which an imbalance between the light energy which is absorbed by the photosynthetic apparatus and the light which can be used to photosynthesize take place. Under these conditions, antioxidant systems must be active to avoid oxidative stress. Nowadays, with the thesis entitled "Extension and importance of winter photoinhibition in vegetal kingdom", the relation between winter photoinhibition and ageing is being elucidated. The model plant to carry out this study is the european mistletoe (*Viscum album*) in which all the surface (stems and leaves) is photosynthetically active and in which the stem can be easily divided in segments depending on the age. The main result of this study is that with an age increment, there is a reduction in winter photoinhibition. Concomitantly there is also a diminution in antioxidant concentration. Thus it can be concluded that under winter stress, ageing is a synonym of enhancement of photosynthetic efficiency.

# Behaviour of the bacterial community of the activated sludge in wastewater treatment plants.

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KEY WORDS: activated sludge, GFP-tagged bacteria, bacterial community, pyrosequencing

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The principal goal of the wastewater treatment by activated sludge is to remove gross solids and to reduce the organic matter fraction and the concentration of microorganisms in the effluents. Bacteria are by far the most dominant group of organisms in this type of biological treatment: a lot of bacteria, and among them many pathogenic bacteria, are continuously coming into the plant with the wastewater and others are involved in the treatment itself. However, the fate of allochthonous bacteria along the process and the composition of bacterial community are not definitively and clearly established. In this work, the fate of two enterobacteria (*Escherichia coli* and *Serratia marcescens*, both expressing a Green Fluorescent Protein [GFP]) was studied and the bacterial composition of the different sections was determined along a secondary treatment by activated sludge.

The assays with the tagged bacteria were done both, in closed systems and in a miniaturized wastewater treatment plant (MWWTP). The joint analysis of the results obtained for both experiments indicated that, the physico-chemical characteristics of wastewater do not affect the permanence of these bacteria. Our results denoted that the microbial populations of a WWTP are involved in the reduction of the density of the GFP marked allochthonous bacteria, highlighting the importance of predation by protozoa. Thus, the density of both tagged bacteria in the secondary effluents decreased more than 70% with respect to those introduced in the primary effluent. Moreover, the fraction that remains in the system was differentially distributed between aqueous and solid phases depending on the bacteria. So, while the remaining *E. coli* cells were concentrated in the flocs and sludge, *S. marcescens* was equitatively distributed between the aqueous and the solid fraction.

To study the composition of the bacterial community of the primary effluent, water and flocs from the aeration tank and secondary effluent of Crispijana WWTP an analysis was carried out using 16S amplicon sequencing, with the Illumina HiSeq 2000. The results pointed out the diversity and complexity of the bacterial communities of these secondary treatment systems and revealed a clear change in the community composition along the treatment. Thus, the primary effluent was characterized by the lowest diversity and the bacterial community structure that differed totally from the rest of samples taken along the treatment. Thus, the water that leaves the plant was formed by a little fraction of bacteria that entered to the WWTP with the primary effluent and bacteria that inhabited in the activated sludge.



# Effects of temperature on the functioning of headwater streams in Northern Spain

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KEY WORDS: stream, decomposition, temperature, leaf quality, decomposers, detritivores.

The main issue of the research group is the study of the functioning of freshwater ecosystems. Temperate forest headwater streams are heterotrophic systems where organic matter inputs from surrounding vegetation are essential to maintain aquatic ecosystem. The organic matter decomposition is a key process in these fluvial systems since it acts as energy and matter transfer across trophic levels, controls nutrient cycling and highly contributes to the global carbon cycle by the release of CO<sub>2</sub>. Despite the generated interest due to predicted global warming, the temperature effects on headwater stream functioning are poorly known, in particular when it interacts with other factors (e.g. riparian vegetation, biota). The aim of the present project -RIOTEM- is focused on the effects and implications of temperature on the stream ecosystems functioning of Northern Spain through the response of leaf litter decomposition and its associated variables. Two recent studies:

1. **To assess whether leaf quality regulate the temperature effect on litter decomposition in headwater streams.**

For this objective, leaf litter of three autochthonous species: alder (*Alnus glutinosa* (L.) Gartner), oak (*Quercus robur* L.) and beech (*Fagus sylvatica* L.), that differ from each other in their initial quality (nitrogen, phosphorous and recalcitrant carbon), were incubated in 3 streams with different mean winter temperature (range: 4.3 - 8.8°C). To distinguish the contribution of decomposers and detritivores fine- and coarse-mesh bags (0.5 and 5 mm) were used. The decomposition rates of highest leaf quality (alder) were faster in all streams for both mesh sizes and it was explained by different microbial oxygen consumption and detritivore colonization. Moreover, they were always higher for the high quality species (alder, oak). Water temperature did not enhance the microbial decomposition rate. However, the breakdown rate (microbial and invertebrate activity) of alder and oak showed a positive trend with temperature that probably responded to differences in benthic shredder among sites since it was observed and change in detritivores density as well as a change in the community composition of shredders related to their thermal regimes. The results suggest that with the increasing temperature predicted by climate change, the type of riparian vegetation could condition the efficiency which the allochthonous organic matter is used.

2. **To assess the temperature effect on the microbial decomposition and its associated aquatic hypomycete assemblages as well as possible synergies with a shift in vegetation of the catchment.**

With this aim, alder (*Alnus glutinosa*) and eucalyptus (*Eucalyptus globulus*) were incubated in three streams differing in their thermal regime. Simultaneously, under controlled laboratory conditions, leaf litter conditioned in these streams were incubated at 5, 10 and 15°C. This experimental design not only will allows us to isolate the temperature effects and eucalyptus plantations from other environmental factors, but also enables to test whether the fungal assemblages adapted to different thermal regimes respond in the same way to shifts in temperature.

# Endocrine disruption and its effects on reproduction in thicklip grey mullets of the Basque Coast.

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KEY WORDS: Endocrine disruption, intersex, mullet, xenoestrogens, waste water treatment plant, environmental monitoring

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Endocrine disrupting chemicals (EDCs) are a group of diverse compounds, most of them artificially synthesized organic chemicals, that interfere with the functioning of the endocrine system, causing reproductive and developmental disturbances in aquatic wildlife.

In the last years, the research group Cell Biology in Environmental Toxicology has performed several studies on the effects of endocrine disruptors on the reproduction of the pollution sentinel species thicklip grey mullet (*Chelon labrosus*) in the Basque Coast. As a continuation of this work, the present PhD work began with the characterization of the reproductive cycle and the gametogenic stages of grey mullets in Basque harbours and estuaries. Intersex males showing previtellogenic oocytes in their testis and elevated transcription levels of vitellogenin (*vtg*) and aromatase (ovarian *cyp19a1* and ovarian *cyp19a2*) genes were detected in male fish from Gernika, Pasaia, Deba, Arriluze, Ondarroa and Santurtzi. Levels of EDCs (estrogenic hormones, polycyclic musks, bisphenol-A, phthalates, alkylphenols and pesticides) were determined in water and fish bile, and high EDC loads were related to the prevalence of intersex or to the levels of biomarker gene transcription detected in the studied populations.

Many of the EDCs suspicious of generating the xenoestrogenic feminizing responses detected are released from waste water treatment plants (WwTPs) receiving urban and industrial waste waters. Thus, we have further studied the effects of effluents from two different WwTPs relevant in the Basque Coast. With this purpose, juvenile mullets were exposed under controlled laboratory conditions to different dilutions of effluent waters from Galindo and Gernika WwTPs during 2 and 10 days. Again, vitellogenin and aromatase gene transcription levels were assessed, in liver and brain respectively, in the exposed fish as sensitive early biomarkers of xenoestrogenicity. In all cases a dilution dependent up-regulation of studied genes was identified.

In a parallel PhD study, we have developed a new biomarker of exposure to xenoestrogenic EDCs. A simple electrophoresis of total RNA extracted from the gonad of all different fish species studied, allows identification of the presence of oocytes in the gonads by visualization of 5S rRNA transcript. This is enough to distinguish females from males, and even intersex individuals. The reproductive stage of females can also be identified with this method. Consequently, 5S rRNA is not only a powerful biomarker of reproductive endocrine disruption in fish gonad, but it can also be used as sex and reproductive marker, which could find several applications in the study of fish stock dynamics.

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# Individual growth evaluation of the earthworm *Eisenia andrei* at low density in horse manure

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KEY WORDS: *Eisenia andrei*, growth, tagging, vermicomposting.

Urban solid waste disposal remains largely unresolved. Vermicomposting appears as an alternative which, in addition, contributes to soil production. *Eisenia andrei* results adequate for this practice due to high growth rates, longevity and early sexual maturity. Nevertheless, large interindividual growth differences within this species as well as growth dependence on population density would require selection of specimens in order to set a sustainable waste management scheme. Literature on *Eisenia* sp as a vermicomposting agent is vast, but individual growth studies within a population are absent. Since tagging soft body organisms presents limitations, our aim in this study has been standardizing the use of fluorescent elastomers as a tagging method in *E. andrei* in order to achieve individualized monitoring. Elastomers remain in the earthworm body for 3 months in 75% of the cases. Mortality associated to the method depends on body size: between 80 to 270 mg survival increases from 45 to 80 %, reaching 100% in specimens larger than 270 mg. The procedure allows us to follow, in short term experiments (3 months), individuals growth patterns. Using a 0.02 ind/g density population and a size range from 80 to 270 mg we found 84 % of the specimens (n=20) showed asymptotic growth. Of them, 16 % correspond to early breeders characterized by high growth rate (0.256) but lower size attained (maxima  $\approx$  323 mg of live weight). The bulk of worms (68 %), exhibited lower growth rate achieving, nonetheless, higher maximum size (597 mg of live weight) due to a longer somatic growth phase. The remaining 16% (n=4) corresponds to specimens with an exponential growth trend on which maximum size has not been obtained. This result is consistent with the idea of selecting parental lines that emphasizes either reproductive or somatic growth.

# Parasitoid Hymenoptera, developmental model and application in Forensic Entomology

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KEY WORDS: Parasitoid, Development, *Nasonia vitripennis*, Pteromalidae, Forensic Entomology.

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Parasitoidism is an interespecific relationship in which the parasitoid adult actively searches for a host to ovoposit on. The resulting immature stages of the parasitoid will feed on the host, killing it in the process. Many parasitoid hymenopterans infest pest and necrophagous species, making them of big interest for biological pest control and Forensic Entomology. More than a half of the known species of the order Hymenoptera are parasitoids. Parasitoid wasps that parasitize necrophagous dipterans often need more time to complete their life-cycle than their hosts, which makes them suitable candidates for the estimation of the *postmortem* interval. In order to use parasitoids for this purpose, it is important to expand our knowledge about their biology, development and geographic distribution.

Our team is trying to determine the diversity and the distribution of the forensically relevant parasitoid hymenopterans in the Basque Country. This knowledge is vital when attempting to use these insects in biological pest control or in forensic cases. One of the most important parasitoid hymenopterans species is *Nasonia vitripennis*, a small wasp of the Pteromalidae family found worldwide. Our goal is to establish its developmental model by rearing it at different environmental temperatures and to find out if the usage of different host species alters that pattern. Furthermore, we intend to use data from carrions in field studies to contrast them with the developmental model extracted from the laboratory experiments and ultimately determine the potential use of parasitoid species in the calculation of the *postmortem* interval in forensic cases.

# Genes involved in skin pigmentation and their association with melanoma

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**KEY WORDS:** *Pigmentation, melanoma, MC1R, SLC45A2, DEFB103*

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Skin color is one of the most conspicuous examples of the biological adaptations to the environment that anatomically modern humans have gone through. We are interested in the study of the genetic variation associated with skin pigmentation variability in order to infer its adaptive value. Besides, we are also interested in investigating whether these variants are also related with susceptibility to melanoma, a skin cancer which is determined by both genetic and environmental factors (i.e. levels of skin pigmentation and intensity of solar irradiation). Therefore, we aim to analyse the genetic diversity (single nucleotide polymorphisms -SNPs- and copy number variants -CNVs-) of some candidate loci that may be related to human skin pigmentation variability in individuals with different levels of pigmentation, as well as in melanoma patients. Furthermore, the adaptive value of these polymorphisms and their potential biomedical implications are assessed using bioinformatic methods for detecting the action of recent positive selection.

We have found some SNPs associated with lighter pigmentation and higher risk to melanoma susceptibility in European populations. In particular, we have provided strong evidence that the derived allele V60L of the melanocortin 1 receptor (*MC1R*) locus and the derived allele 374F of locus solute carrier family 45 member 2 (*SLC45A2*) have been under recent positive selection in South European populations and that their frequencies are higher in regions with lower UV irradiation intensity. We have observed, however, that these alleles also confer a higher susceptibility to melanoma. These observations, therefore, support the adaptive value of the human skin depigmentation and are examples of how an adaptive process (depigmentation in zones with less solar irradiation) can help to maintain an allele related with susceptibility to disease (melanoma susceptibility). We are also investigating the putative role of beta-defensins in human pigmentation. For that purpose, we are analysing *DEFB103*, which is variable in copy number (CNV), in order to find relevant polymorphisms that might also be responsible for human pigmentation variability.

# Fisika eta Ingeniaritza Elektronikoa



Física e  
Ingeniería Electrónica

# Desing of integrated Circuits for Computational intelligence.

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KEY WORDS: Intelligent Environments, Soft Computing, Field Programmable Gate Arrays, Integrated Circuits, Embedded Systems.

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In recent years much effort has been devoted to research in the field of Intelligent Environments. This recent paradigm which is also known as "Ambient Intelligence (Aml)", proposes environments (e.g., public or private halls, rooms or spaces) endowed with a set of electronic systems that are able to adapt to the preferences and necessities of the people existing in them in order to make their daily activities more easy and comfortable. To cope with these special skills, these systems usually have used computational intelligence paradigms such as fuzzy systems, neural networks or genetic algorithms.

One of the requirements for achieving this goal in its broadest sense, is certainly, the availability of small-size, low-cost and low-power electronic devices with also high processing speed as they act in a scenario that requires real-time response. However, such features are quite compatible with the high computational requirements of the abovementioned intelligent paradigms. As a result, most existing solutions are basically PC-based, because they focused more on the feasibility of the models, rather than on their physical implementations. An embedded system for Intelligent Environments has been proposed by our group in as a solution for achieving efficient implementations of these systems. The system was implemented in a Field Programmable Gate Array (FPGA) which is an integrated circuit designed to be configured by the customer or designer after manufacturing.

Another important advantage provided by the FPGAs is the possibility of implementing the entire system in the same device, these systems are called System on Programmable Chips (SoPC). This is achieved using Soft microprocessors, that is, microprocessors implemented using the elements of the FPGA. That means it is possible to implement Software partitions in the FPGA.

## **Dynamical Partial Reconfiguration**

Dynamical Partial Reconfiguration (DPR) is a feature that allows modifying dynamically a part of the logic of an FPGA while the rest continues operating without interruption. This ability makes it possible to mutiplex many different functions in time, similar to the feature of a microprocessor to switch tasks in a multi-task single-processor system. Thus, a functional block (block of logic) is implemented or deleted in the FPGA according to the needs of the system. The benefits of this recent technology are very noticeable:

- Size reduction of the FPGA device required to implement a given function and therefore reductions also in cost and power consumption.
- More flexibility to select among different algorithms for a given application.
- Improving FPGA fault tolerance.
- Accelerating configurable computing.

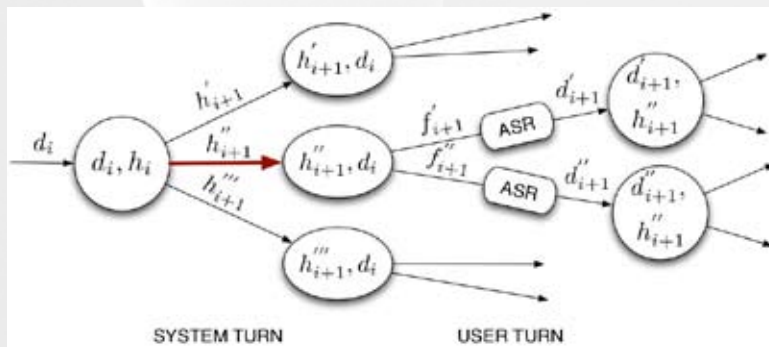
# Spoken Dialog Systems based on Probabilistic Finite State Bi-Automata

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KEY WORDS: spoken dialogue, pattern recognition, statistical dialogue manager

The new Interactive Pattern Recognition (IPR) framework has been proposed to deal with human-machine interaction. In this context a new formulation has been recently defined to represent a Spoken Dialogue System as an IPR problem. In this work this formulation is applied to define graphical models that deal with Spoken Dialogue Systems. The definition of both a Dialogue Manager and a User Model are shown and the estimation of the parameters and smoothing techniques are presented in the paper. These models were evaluated in a dialogue generation task on two very different corpora: Dihana corpus consisting of Spanish spoken dialogues acquired with the Wizard of Oz technique and Let's Go corpus consisting of spoken dialogues in English between real users and the Ravenclaw dialogue manager developed by CMU. The results obtained show that original and simulated dialogues exhibited very similar behaviours, thus demonstrating the learning capacity of the proposed models in both a controlled Wizard of Oz task and a spoken dialogue system that interacts with real users. This formulation can then be considered as a promising framework to deal with Spoken Dialogue Systems.

In this work the probability distributions associated to both, the Dialogue Manager and the Simulated User are modeled through a graphical model consisting of sets of states representing (h,d) pairs. Some of the states of this



model correspond to the DM and are labelled by (d,h'), being d the output of the Speech Understanding system given the user feedback f and h' the system hypothesis at the previous interaction. The states corresponding to the user, are labelled by pairs (h,d') where h is the system hypothesis and d' is the deterministic decoding of the previous user feedback f'. An example of such a model is illustrated in the figure on the left. The edges that connect a DM node with different SU nodes represent the

different possible hypothesis that can be chosen in a system turn and each of them has associated a probability  $P(h|d,h')$ . Additionally, each state need to be labelled by the values of all the relevant internal variables and the uncertainty rate when speech is considered, thus leading to an attributed model. This information is typically associated to domain-specific frame-and-slot templates used in dialogue systems. In the same way edges connecting a SU node with different DM nodes represent possible user feedbacks according to the SU probability distribution.

## Model Estimation

The parameters of the model can be estimated in a three step learning procedure as follows:

- Get a dialogue corpus consisting of pairs of user and system turns. Then get an initial maximum likelihood estimation of the parameters of both DM and SU models.
- Define a DM strategy and several SU behaviours. Define also error recovery strategies. Run the system until desired dialogue goals are successfully achieved for different simulated user behaviours.
- Run the SDS with real users while using adaptive learning to obtain a DM adapted to real interaction feedbacks.



# Language and Speaker Recognition: Contributions to Modeling and Robustness Against Channel and Environmental Noise (GTTS, mireia.diez@ehu.es)

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KEY WORDS: Speaker Recognition, Language Recognition, Phone log-Likelihood Ratios

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The research carried out in the framework of the Ph.D project entitled “Language and Speaker Recognition: Contributions to Modeling and Robustness Against Channel and Environmental Noise” has been developed with the Software Technologies Working Group (GTTS). The work focuses on two of the main research fields of the group: language and speaker recognition.

## LANGUAGE AND SPEAKER RECOGNITION

These two tasks consist of recognizing a language/speaker given an audio signal containing a voice utterance. Both tasks are accomplished by completely automated systems, without human interaction. The applications of these systems cover several possibilities: Forensic applications, automated consumer advice telephone-based systems, automated information searching and indexing in TV broadcasts, meetings and other multimedia resources, telephone call filtering...

Both tasks share a common main system structure: First of all, a speech dataset should be split into three different subsets: training, development and test. The first step consists of extracting a set of features to characterize the language or speaker (traditionally low-level acoustic or high-level phonotactic ones) for the different data subsets.

Training data is then used to estimate the language/speaker models. On the next step, the development set is evaluated against the models, producing a set of scores. These are then utilized to estimate calibration parameters. The calibration is a linear transformation, applied over scores to minimize system's cost over all possible operating points. Finally, each test utterance is evaluated against each model, producing a score which is then calibrated. The final score is then used to make a final decision. Among different contributions done on the thesis project, one of the highlights would be the introduction of a new set of features usable for both, language and speaker verification: Phone Log-Likelihood Ratios (PLLRs).

## PLLR FEATURES

PLLRs convey short-term acoustic and phonotactic information, and take advantage of some goodness of high and low level features: they are frame-level features, easy to extract, with several possibilities to be plugged into state-of-the-art systems and their phonetic basis gives them robustness against noise and channel noise.

The basis of the features would be the following: Given a phone decoder including  $N$  phone units, an  $N$ -dimensional vector  $\mathbf{p}$  of phone posterior probabilities can be estimated at each frame. The vector  $\mathbf{p}$  defines a certain mixture of phones, the one that, best describes the spectral content of the analysis window. These features can be then transformed into phone log-likelihood ratios, which carry the same information, but feature more Gaussian distributions making them more suitable for the modeling.

The use of this set of features has proven to be a fruitful way of extracting information from speech utterances, providing significant performance gains with regard to state-of-the-art phonotactic and acoustic systems, on standard benchmarks widely used by the research community on language recognition. The system has also revealed a complementarity when fused with both kinds of systems, achieving even further performance improvements. This is also a new way of making use of phonetic information for speaker recognition, complementary with the state-of-the-art acoustic systems.

# Magnetolectric effect in new laminated composites

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KEY WORDS: Magnetolectric effect, magnetostriction, piezoelectricity, piezoelectric poliimides

The magnetolectric effect (ME) is defined as the electric field (or voltage) induced under the application of a magnetic field (direct ME), or vice versa, the magnetic induction arising under the application of an electric field (inverse ME).

Research on magnetolectric laminated composites has increased in last years, mainly due to the potential applications in magnetic field sensors [1,2], current sensors [3], transformers [4] and microwave devices [5], among others. One of the most used structures for these composites is the L-T one, where a piezoelectric film polarized along its thickness direction is glued between two magnetostrictive ribbons, which are magnetized along the length one. An applied ac magnetic field elongates and shrinks the magnetostrictive ribbons. That deformation goes through the piezoelectric film, inducing a voltage.

These magnetolectric laminated composites are fabricated using Fe based amorphous alloys as magnetostrictive elements and two different polymers, PVDF and a new series of high temperature copoliimides, as piezoelectric films.

The aim of our work is to develop small magnetolectric sensors (0,5-1 cm long) with a high magnetolectric response and keep that response constant up to 100 °C. This fact would allow us to use such sensors at frequencies around 400 kHz, suitable for near field communications.

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# Fabrication of magnetic nanodisks by self-assembled templates

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KEY WORDS: magnetic nano-disks, self-assembling, nano-fabrication.

The fabrication based on self-assembled templates is presented as a simple, high-throughput, and parallel processing to obtain magnetic nanostructures. Apart from their scientific interest, these structures can be used in promising biomedical applications, such as cancer therapies (magneto-mechanical actuation and hyperthermia), Magnetic Resonance Imaging (MRI), magnetic detection of specific targets, and drug delivery [1]. The lack of remanence of magnetic disks in vortex state solves agglomeration problems, still allowing magnetic actuation at moderate fields. Three different techniques to fabricate Permalloy (Py) nanodisks with magnetic vortex state are investigated:

1) In the self-assembling latex sphere technique, the homemade spheres are deposited by spin-coating over a Py thin film sputtered onto Si substrates. The spheres, assembled in ordered monolayers, are subsequently reduced in size by reactive ion etching in an oxygen atmosphere. The remaining pattern of spheres is used as protective mask for creating Py nano-disks by ion-etching the Py film [2].

2) Anodized alumina membranes are prepared by a double-step oxidation process, and the ordered hole pattern obtained is used as a template for Py disks. Py thin films are deposited either by physical vapor deposition or by pulsed electrodeposition. After deposition, the alumina membrane is dissolved to release the Py nano-disks [3].

3) Hole-mask colloidal lithography utilizes a PMMA sacrificial layer coated with a positively charged PDDA polyelectrolyte to obtain a very homogeneous pattern of self-assembled functionalized PS beads. These beads are then covered by a thin Cr layer that is tape-stripped to reveal a hole pattern. The Py disks are deposited within the holes [4].

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# Thin-film microsensors based on giant Magneto-Impedance

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KEY WORDS: Magneto-Impedance, Thin-Films and Sensors

## INTRODUCTION

The Magneto-Impedance (MI) is the change of the electrical impedance of a soft magnetic conductor when a magnetic field is applied. This is an extremely sensitive effect than can be used for developing low field magnetic sensors, with resolutions down to the pT range [1]. Thin film-based structures are preferred over wires and ribbons because can also be fabricated using standard techniques of the microelectronic industry [2]. For achieving a useful MI response, the magnetic film has to be rather thick (about 1  $\mu\text{m}$  for frequencies of 1 GHz). However, in sputtered Permalloy (Py) films, the magnetic softness is deteriorated when thick films (over 200 nm) are deposited due to the appearance of the “transcritical state”. To overcome this issue multilayered structures were developed by stacking several Py films below the critical thickness, separated by thin Ti spacers intended to interrupt the “transcritical state”. Additionally, it is possible to increase the MI performance using sandwich structures where a non-magnetic conducting layer placed between two magnetic layers. The research to optimize the properties of the materials and to develop an optimum multilayered sandwiched (MS) structure is described elsewhere [3].

## EXPERIMENTAL

Micro-shaped GMI elements have been prepared by sputtering with a multilayered and sandwiched structure, and patterned by lift-off in the form of stripes with different lengths (0.5 to 2.0 mm) and widths (70-130  $\mu\text{m}$ ). A second photolithography process defines contacts at the ends of the samples so they can be inserted in a microstrip line. Its magneto-impedance has been measured as function of the applied magnetic field (up to 150 Oe) and the frequency (up to 300 MHz) using a network analyzer. Also a dedicated electronic circuit with different detectors and MI elements has been tested and measured its noise level to determine the minimum magnetic field that can be detected.

## RESULTS AND DISCUSSION

A maximum value of 150 % for the magnitude of the MI and 60 %/Oe of the sensitivity to the applied field has been found for the sample 110  $\mu\text{m}$  thick and 1 mm long. Both figures of merit strongly depend on the aspect ratio of the sample through the magnitude of the effective anisotropy [4], the quality of the patterning, and the distribution of current in the sample. The evaluation of the performance of the microsensors is completed with noise analysis. After proper matching of the MI sample in the electronic circuit, white noise values of about 120 pT/  $\text{Hz}^{1/2}$  are obtained.

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# IZPILab: RF and Control Applications for Particle Accelerators

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KEY WORDS: RF instrumentation and control, beam diagnostics, particle accelerators, EPICS.

Researchers from the RF and Microwaves, and the Automatic Control Group of the Department of Electricity and Electronics s have founded IZPILab, a joint Beam Laboratory for the development of Electronics, RF and Control Applications for Particle Accelerators, including beam generation, beam transport and beam measurement and diagnostics. The research activities refer to problems, both from basic science and from applied science and technology in the field of Particle Accelerators, where RF and control play a relevant role. Current projects include the development of beam sources, beam diagnostics, RF devices and controls, and the corresponding electronics.

## EPICS AND DISTRIBUTED CONTROL SYSTEMS

EPICS (Experimental Physics and Industrial Control System) is a set of Open Source software tools, libraries and applications developed collaboratively and used worldwide to create distributed soft real-time control systems for

scientific instruments such as a particle accelerators, telescopes and other large scientific experiments. Goals of the group using EPICS:

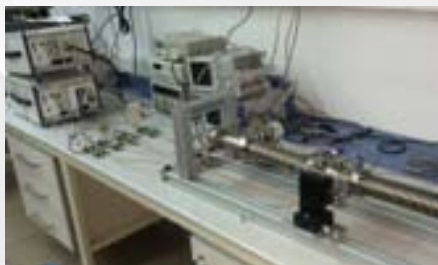
- To integrate modern control standards in a single system for scientific facilities together with usual automatic control tools.
- To develop this middleware to get an efficient and secure communication between all devices, redistributing messages and requests.
- To compare different EPICS developments and solutions, using hardware test-benches.
- Integration into an EPICS net of some common diagnostics and control devices (BPMs, LLRF) widespread in Particle Accelerators.

The research group has started a collaboration with the research center Centro de Laseres Pulsados UltraCortos Ultraintensos (CLPU) of Salamanca for development and integration of EPICS networks.

## PARTICLE ACCELERATOR SCIENCE AND TECHNOLOGY

The group is involved in several projects for particle accelerators. Among these it is worth mentioning:

- Beam diagnostics and related electronics: active projects are related with Beam Position Monitors, for highaccuracy measurement of beam bunches position; Integration between EPICS and the RF Cavities control system; Beam profile diagnostics based on secondary electron emission.



- Beam generation through compact new generation microwave-driven ion sources.
- RF Instrumentation and Control: In an RF accelerator, the particles are accelerated by RF fields with appropriate amplitude and phase, through a high power transmission chain comprising a wide range of control systems. The research group is working on:

1. Low-Level RF controls of frequency, amplitude and phase of accelerating RF signals injected into the particle accelerating structures and to get linear and spurious-free behavior of RF transmitters
2. RF subsystems to optimize RF signal injection in RF cavities for plasma generation or particle acceleration
3. Experimental characterization and conditioning of low and high power RF devices and subsystems

# Magnetic Symmetry in the *Bilbao Crystallographic Server*

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KEY WORDS: magnetic symmetry, magnetic structures, phase transitions.

The *Bilbao Crystallographic Server* ([www.cryst.ehu.es](http://www.cryst.ehu.es)) is a free website containing databases and interactive computer programs about various crystallographic subjects: crystal-structure symmetry, phase transitions, solid state problems, etc. It has been constantly growing since it was created in 1997, incorporating new programs and databases, which are distributed in shells. Recently, this research group has developed a new shell devoted to magnetic symmetry, which contains 4 programs devoted to magnetic symmetry; some others are still ongoing.

In a phase transition where the low-temperature phase has magnetic properties, some atoms (in particular those with unpaired electrons at 3d and 4f orbitals) can acquire spontaneous non-zero magnetic moments; the time-reversal symmetry is not conserved, as it was trivially conserved in non-magnetic structures. Thus, the symmetry operations leaving invariant the low-temperature magnetic structure can be accompanied by a time-reversal operation. Therefore, it is necessary to consider the presence or absence of the time-reversal operation together with the symmetry operations of the conventional space groups. Thus, the 1651 magnetic space groups are derived, which are necessary to describe magnetic structures.

The developed programs enable the use of magnetic symmetry to describe and resolve magnetic structures. When resolving magnetic structures, magnetic symmetry considerations have been historically ignored on behalf of the representation analysis, mainly due to the lack of appropriate tools to deal with the complexity of magnetic symmetry groups. One of the reasons to develop the magnetic symmetry shell is to ease the use of symmetry in magnetic phase transitions, which is a complementary alternative to the representation analysis method.

The *Bilbao Crystallographic Server* programs devoted to magnetic space groups and magnetic phase transitions developed by the research group are:

1. **MGENPOS** and **MWYCKPOS**. Databases of general positions and Wyckoff positions of magnetic space groups.
2. **MAGNEXT**. A program to derive the unpolarized neutron magnetic diffraction systematic absences. Despite not having the same resolving power than the systematic absences for X-ray diffraction, the magnetic systematic absences are useful to find the magnetic space group and therefore to resolve structures.
3. **MAXMAGN**. List of maximal magnetic space subgroups of conventional space groups compatible with a given propagation vector. The target of this program is to provide a list of all the maximal non-conjugated subgroups of the group of the paramagnetic phase in a magnetic phase transition, making use of the symmetry restrictions imposed by the propagation vector. These subgroups are the only ones that are allowed to describe the symmetry of the magnetic structure.

The next program to be published is a collection of real magnetic structures taken from the literature which makes use of the already developed programs to provide interesting crystallographic data and downloadable material (pictures, cif files, etc). Some other programs are also ongoing or arranged: databases of crystal non-magnetic tensors (TENSOR) and magnetic tensors (MTENSOR), a database of normalizers of magnetic space groups, and domain-related programs.

# Everything You Always Wanted to Know About Perovskites\* (\*But Were Afraid to Ask)

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KEY WORDS: perovskite, structural phase transition, symmetry adapted modes

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One of our research fields is the crystal structure and phase transition studies of the double Perovskites materials, which have the general formula  $AA'BB'O_6$ . Many combinations of the cations have been used giving rise to a long series of materials.

The phase diagram (Figure 1), which represents the tolerance factor values versus the transition temperature for each material, is constructed based on long process, starting by the chemical synthesis, then checking the samples, performing good experiment (XRD, NPD or Synchrotron), analysis data, refining the structures at room temperature using Rietveld method in order to get the RT space group. The same process should be repeated for high and/or low temperature in order to get the transition temperatures and the phase transition sequence. The important point of is this kind of diagrams, it that it allows the extraction of general, common and not common features of the materials.

The different combinations of A and B cations gives rise to very innovator materials with interesting applications (Na and Li batteries, Multiferroic, devices...). In our research field more techniques were using depending of the cation combination we are working on, for instance SEM, TEM, NMR, Mossbauer...)

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# Plasmonics of metallic nanoparticles linked by molecular structures: optical and transport properties

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KEY WORDS: nanophotonics, plasmon resonances, molecular linkers

We study theoretically the electromagnetic response of metallic nanostructures, free-standing or supported on surfaces, when they are excited by external sources such as electron beams (electron microscopy) or light (optical spectroscopy). In both cases, resonant oscillations of free electrons, called plasmons, emerge in the nanostructures. From a basic research perspective, these systems are very interesting since their optical properties differ from the optical response of the same metallic material in the bulk. On the other side, these systems are the basis for applications such as sensing, surface-enhanced spectroscopies, cancer therapies, renewable energies or active devices.

In particular, we have studied the relation between the optical properties and the transport properties of a hybrid nanostructure consisting of a chemically synthesized metallic nanoparticle dimer connected by a molecular structure. Our goal is to achieve a better understanding of the complex connection between the electronic transport through molecular linkers and the changes in the optical extinction spectra of the connected dimers in the visible and near infrared frequencies.

The molecular linker connecting the dimer has been modelled with increasing complexity. First, it has been considered as a cylinder with a purely conductive nature, which helps to understand the main spectral trends of the emerging plasmon modes [1,2]. In a second step, a more realistic dielectric response of the linker has been considered, taking into account the excitations of the connecting molecules. This leads to a more complex optical response involving the interaction of the plasmon cavity modes and the excitons from the molecular transitions [3]. Finally, the possibility of an ensemble of molecules entirely covering the nanostructure is considered as well [4]. In comparison to the case when the molecules are placed only in the interparticle gap, for the entirely covered dimer a new resonance emerges, arising from the interaction of the plasmon cavity modes and the geometrical modes of the molecular aggregate shell.

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# Positrons live fast, die young!

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KEY WORDS: positron annihilation lifetime spectroscopy, shape memory, alloys, polymers, biological membranes, cancer.

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The lifetime of a positron in matter - gas, liquid, or solid - depends on its electronic environment and this in turn tells us much about the submicroscopic nature of the material. We measure the lifetime of positrons using positron annihilation lifetime spectroscopy (PALS). PALS is a non-destructive technique to study voids and defects in solids and soft matter at the subnanometer level. Our study covers material physics, biophysics and cancer research.

## OUR GOALS

- To determine the vacancy concentration, defect type and dynamics in **shape memory alloys** and **topological insulators**.
- To study the relation between shape memory and free volume properties in **polymers**.
- To define the effect of nanoparticles in the free volume of the **nanocomposites**.
- To analyze the effect of ceramide in the free volume void size inside **biological membranes**.
- To measure the mean intermolecular space of 3D living **cancer cell** cultures.

Geologia



Geología

# Contribution to the study of the titanosaurian dinosaurs from the Late Cretaceous of southern Europe

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KEY WORDS: titanosaurs, dinosaurs, Europe, Late Cretaceous, palaeobiology.

Titanosaurs were the most successful group of sauropod dinosaurs from the Cretaceous, with a global distribution and including the only survivors of the group to the end of the Mesozoic. So far, more than 60 valid species are known, which include both dwarf species and the biggest animals that have ever walked on the Earth.

At the end of the Mesozoic (ca. 80-66 M.y.), Europe was an archipelago with an interesting continental faunal evolution and distribution. Up to now, three titanosaurs are well-known in one of these islands, the Ibero-Armorican Island (Iberian Peninsula and France in the Late Cretaceous): *Lirainosaurus astibiae*, *Ampelosaurus atacis*, and *Atsinganosaurus velauciensis*. *Lirainosaurus* is a small Iberian sauropod (6-8 meters in body length) recorded in the Campanian-Maastrichtian of Laño (Treviño County) and Chera (Valencia). *Ampelosaurus* and *Atsinganosaurus* are represented in southern France sites from the end of the Cretaceous. Both are larger than *Lirainosaurus* (ca. 12 meters). However, it is still very difficult to assess the actual titanosaurian biodiversity of the Ibero-Armorican Island. The discovery of new fossil-sites in southern France and central Spain shows that the titanosaurian diversity in the Ibero-Armorican Island was much higher than currently thought, with at least five different species. Two localities are of special interest, as their study seems to confirm this hypothesis. In Cruzy (Languedoc), a rich vertebrate assemblage has been recovered since the 1990s, with numerous titanosaurian remains that represents indeed a fourth genus. On the other hand, the locality of Lo Hueco (Cuenca) has yielded some thousands of isolated bones and more than twenty sets representing partial skeletons of several titanosaurian individuals. A preliminary analysis of the diversity based on isolated elements indicates the presence of, at least, three morphotypes of titanosaurs, probably belonging to two different taxa.

The relationship of these titanosaurs with previously described and among them is yet to be defined. The systematics of the European titanosaurs will be studied in a short-termed project, which will also help in the assessment of their palaeobiogeography and their migrations in Laurasia. The use and application of new techniques, as the CT-Scans, Scanning Electron Microscope or geochemistry, greatly improve and enhance the classical approach to the study of the fossil-bones: reconstruction of the brain, observation of microwear patterns in the wear facets of the teeth, palaeohistology, hypotheses about their food preferences, etc.

For example, the results obtained about this higher diversity are coherent with others about the crown morphotypes of the teeth of adult titanosaurian individuals. In addition, an exhaustive study of the microwear patterns of the wear facets of these teeth showed up divergences and differences between the taxa, and suggests that the adult titanosaurs had different food preferences. Significant differences in size as well as in tooth shape strongly suggest that the various titanosaurs from southwestern Europe were adapted to different ecological niches. To sum up, this information is of great value for taxonomical and palaeobiological purposes.

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# Geological record of the recent anthropogenic impact on salt marshes from the eastern Cantabrian coast

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KEY WORDS: foraminifera, salt marsh, sedimentary record, human occupation, natural regeneration, environmental management, sea-level rise

Analysis of 14 short sediment cores (up to 50 cm) and 71 surface samples from different salt marshes in the Urdaibai, Plentzia and Santoña estuaries in the eastern Cantabrian coast, provided key information to define criteria to distinguish between areas of natural and anthropogenically-influenced evolution in the sedimentary record. A multi-proxy approach based on benthic foraminifera, sand, organic matter and heavy metal content, together with aerial photography, was developed to characterise the two possible evolution paths. Radiocarbon and short-lived radionuclides ascribed an age to the sediments.

High-marsh surface samples from the Urdaibai estuary (dead foraminiferal assemblages) were used to develop a unimodal-based regression and calibration model that allowed the reconstruction of relative sea level using three cores from the Urdaibai estuary that presented a natural evolution. The vertical errors ranged from  $\pm 6$  to  $\pm 10$  cm. Foraminifera-based reconstructions were placed into a temporal framework using  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$  and  $^{14}\text{C}$  activities and  $^{210}\text{Pb}$ -derived sediment accumulation rates, which permitted the calculation of relative sea-level variations since 1300 CE. These naturally evolved sequences showed abundant foraminifera and an enrichment of metals (Cu, Ni, Pb and Zn) at the surface (at different depths) related to recent industrialisation since the 1910s, but especially since the 1960s. The measured relative sea-level rise rate was of  $2 \text{ mm yr}^{-1}$  during the 20th century (since the inflexion point located around the mid-1920s) and was in general agreement with the nearby Santander tide gauge and the further north Brest tide-gauge record trends, both located in the Bay of Biscay. The reconstructed rate for the 20th century was 4 times higher than the calculated late Holocene background rate since 1300 CE ( $0.5 \text{ mm yr}^{-1}$ ).

The other eleven cores showed an anthropogenically-influenced evolution: regeneration after reclamation due to agricultural occupation, introduction of large sediment loads due to deforestation, and human-introduced allochthonous deposits. The abandonment of agricultural soils (during the 1950s in the Urdaibai estuary, the 1970s in the Plentzia estuary, and the late 1950s and early 20th century in the Santoña estuary) provoked the entrance of estuarine water that caused increasing amounts of sand and benthic foraminifera deposited at high sedimentation rates (average  $14\text{--}18 \text{ mm yr}^{-1}$ ), comparing to the much lower sedimentation rates observed when the salt marshes were being regenerated ( $0.9\text{--}6 \text{ mm yr}^{-1}$ ). This regeneration process was very rapid (around 10-15 years). The regenerated environments showed abundant foraminifera and an enrichment of heavy metals (Cu, Ni, Pb and Zn) (at similar depths) due to recent industrialisation, but also due to dilution during the regeneration process (by mixing with agricultural soils and due to high sedimentation rates), when otherwise metals would also show enriched contents. The regeneration pattern observed is of great utility in order to identify agricultural horizons and the following regeneration process in areas with no aerial photography.

Deforestation caused the introduction of large sediment loads, and the corresponding dilution of foraminifera and heavy metals, changing the topographic elevation, and, therefore, the environment of deposition with respect to the tidal frame (from a tidal flat to a salt marsh environment).

Apart from the two previous human influences, salt marshes can also receive allochthonous sediments as construction sand, which can complicate interpretation of the environment of deposition.

Salt marshes from the eastern Cantabrian coast seem to be able to keep pace with ongoing sea-level rise, due to the abundant regional input of detrital materials, which allows high sedimentation rates as observed in regenerated marshes. The rapid regeneration observed is of great interest for environmental management of modern coastal zones where extensive reclaimed land could be easily restored to tidal wetlands and serve as an adaptation measure against climate change consequences on the coastal zone, as these environments accrete sediment very fast to reach equilibrium with the tidal frame.

# Aptian carbonate platforms from the central area of the Basque-Cantabrian Basin: stratigraphy and geochemistry

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KEY WORDS: Aptian, carbonate platform, Basque-Cantabrian Basin, OAE1a

In this research project, the area South of Bilbao has been studied and the sedimentological, biostratigraphical and geochemical characteristics of its aptian geological record described with the aim of better understanding the events occurred during this period and their correlation with other basins worldwide. These works will be promptly compiled in a PhD Thesis titled “Aptian carbonate platforms from the central area of the Basque-Cantabrian Basin: Stratigraphy and geochemistry”.

The Aptian stage is located within the Lower Cretaceous (125-113 m.y. approx.) and is divided in the Early and Late substages. In this work, the Early Aptian and the transition to the Late Aptian have been thoroughly studied, as well as the uppermost record from the previous Barremian stage. The Aptian is a key period for understanding past climate under greenhouse conditions and a number of geological events, which can be studied through the sedimentary record. Massive volcanic eruptions in the Ontong-Java plateau and global warming, which was enhanced by volcanic degassing, caused disturbances on the Carbon Cycle, such as the OAE1a. The OAE1a is a palaeoceanographic event characterized for a negative spike followed by a positive one in the  $\delta^{13}\text{C}$  curve and associated black shale deposits.

## WORKS CONDUCTED DURING THIS RESEARCH

In this work, several new sections from the central area of the Basque-Cantabrian Basin, south of Bilbao, have been logged and sampled and four geological formations described, particularly the one deposited in a carbonate platform setting. Several key aspects of each one have been studied:

1. **Sedimentology and Stratigraphy:** Each kind of facies has been described both in the field and in thin section. Fieldwork has also allowed us to correlate the different sections.
2. **Biostratigraphy:** ammonite specimens have been retrieved and classified by an expert. This has led to the establishment of a detailed new ammonite zonation for the area.
3. **Geochemical:** TOC,  $\delta^{13}\text{C}_{\text{inorg}}$ ,  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{18}\text{O}$  analysis have been conducted with the aim of identifying palaeoceanographic events such as the OAE1a and organic matter-rich levels.

## CONCLUSIONS AND SCIENTIFIC INTEREST

This PhD project has described the sedimentary record of an, until recent, little-known area. The sedimentological, biostratigraphical and geochemostratigraphical techniques have led us to identify several aptian geological events:

- Changes in the sea level, established through the temporal evolution of the carbonate platforms.
- Changes in the seawater isotopic composition through time and development of OAE1a events.

It is important to establish whether these events are global or local so that the aptian climate is better characterized. The study of the Aptian allows us to better understand the future behaviour of the Earth's climate system in a global warming scenario.

# Materials development for fuel cell power generation (SOFC systems)

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KEY WORDS: Solid Oxide Fuel Cells, Contact perovskite, Ohmic resistance losses.

A solid oxide fuel cell (SOFC) converts chemical energy of a fuel to electricity and heat through of redox reactions; no combustion process is involved. The operating principles of SOFC are based on a combination of a gaseous fuel (hydrogen) and an oxidant gas (oxygen from the air) through electrodes and via an ion conducting electrolyte. Hence, SOFC are clean, reliable and nonpolluting energy sources [1]. High temperature (HT) SOFCs, which operate at 850-1000 °C, offer great promise for stand-alone applications. For smaller scale applications, such as micro-combined heat and power systems (CHP), auxiliary power units (APUs) and small electrical generators, there is a need to lower temperatures of operation, into intermediate temperature (IT) range of 500-800 °C [2]. While significant progress has been made in anode materials with enhanced tolerance to coking and contaminant poisoning, lacks of contact between interconnect ribs and cathode still contributes considerably to energy loss and shorten the durability of the cell. The use of a suitable cathode contact material minimizes the interfacial electrical resistance and maximizes the power output of IT-SOFC stacks. The cathode contact material composition is required to possess high electrical conductivity and appropriate sintering activity to minimize the resistance of the contact layer itself and to protect the steel substrate from excessive oxidation. Besides, it must be chemically compatible with chromia-forming interconnects and the perovskites cathodes [3].

Three perovskites,  $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{Fe}_{0.6}\text{Mn}_{0.3}\text{Co}_{0.1}\text{O}_3$  (LSFMC),  $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$  (LNF) and  $\text{LaNi}_{0.6}\text{Co}_{0.4}\text{O}_{3-\delta}$  (LNC) were investigated as contact materials, using  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$  (LSF) and Crofer22APU as cathode and interconnect, respectively. Phase structure using X-ray Diffraction (XRD), electrical conductivity and thermal expansion coefficient (TEC) values of selected materials were determined. The observed high conductivity values for LNF and LNC and, the good fit between TECs values of LSFMC and the interconnect make the use of these materials as contact layers interesting. The important properties of the resulting {interconnect/contact layer/cathode} systems; including area specific resistance (ASR) and post-mortem studies by scanning electron microscope equipped with a dispersive X-ray analyzer (SEM-EDX) were investigated. The results reveals that there is chromium enrichment in the contact and cathode layers which allows the formation of phases like  $\text{SrCrO}_4$  and Cr-containing perovskites in short exposure times. The contact made by LNC, gives the lowest electrical area specific resistance. An adequate integrity and low reactivity is achieved when LNF contact coating is applied between Crofer22APU and LSF cathode without compromising the contact resistance of the system.

## ACKNOWLEDGMENT

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# Metalloporphyrin-based MOFs: new strategies for catalysts immobilization.

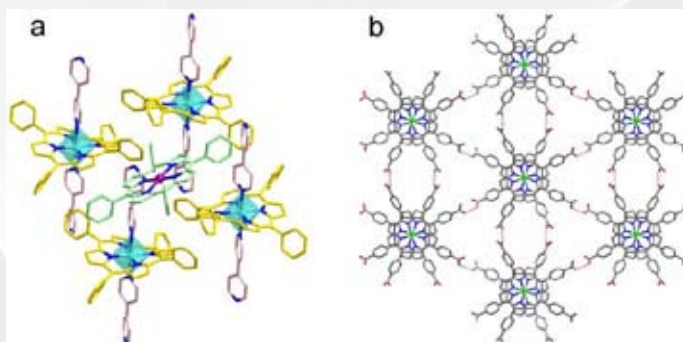
María Isabel Arriortua<sup>1</sup>, M. Karmele Urriaga<sup>1</sup>, José L. Pizarro<sup>1</sup>, Gotzone Barandika<sup>2</sup>, Begoña Bazán<sup>1</sup>, Karmele Vidal<sup>1</sup>, Edurne Serrano<sup>1</sup>, Roberto Fernández<sup>1</sup>, Joseba Orive<sup>1</sup>, Verónica de Miguel<sup>1</sup>, Arkaitz Fidalgo<sup>1</sup>, Aroa Morán<sup>1</sup>, Francisco Llano<sup>1</sup>, Eder Amayuelas<sup>1</sup> and Laura Bravo<sup>1</sup>

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KEY WORDS: Metalloporphyrin, MOF, Catalyst.

Metalloporphyrin systems are one of the cornerstones on which the existence of life is based, as major biochemical, enzymatic and photochemical functions depend on the special properties of the tetrapyrrolic macrocycle.<sup>1</sup> Thus, porphyrin catalysts are well-known to be highly efficient in many catalytic reactions and, during the last years, a great effort has been devoted to the immobilization of distinct types of catalysts on solids.<sup>2</sup>

To that effect, a widely used strategy consists of anchoring the porphyrin catalysts to different supports, such as graphene, gold or other polymeric membranes. However, on the last years the development of porous metalloporphyrinic MOFs introduce the possibility of occupying the cavities presented by these compounds with catalytic molecules. On the other hand, a recent and not much studied strategy consists of obtaining metalloporphyrinic solids, where the MOF itself plays as a catalyst. In this sense, exploring these possibilities we have obtained two different compounds. The first of them, with formula  $[\text{CoTPP}(\text{bipy})] \cdot (\text{CoTPP})_{0.22} \cdot (\text{TPP})_{0.78}$  correspond to a porous metalloporphyrinic MOF<sup>3</sup> (a), where the metalloporphyrinic catalysts were immobilized into the cavities. The second,  $\mu\text{-O} \cdot [\text{FeTCPP}]_2 \cdot n\text{DMF}$ ,<sup>4</sup> is one of the very few porphyrinic systems where the MOF itself plays as a catalyst (b). While the first does not present catalytic activity due to the poor accessibility of the network and the few active centres, the latter exhibits good properties as heterogeneous catalyst.



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Matematika



Matemáticas



# The Ph. D. In Algebra, Mathematical Analysis and Geometry and Topology: Some experiences.

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KEY WORDS: Másteres oficiales, Becas, Información doctorado.

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In this talk, mainly oriented to last years degree students, we review, in a general way, the situation of the predoctoral grants as well as the official masters. Our aim is to facilitate this difficult process to those interested in starting, in the near future, a Ph. D. in Mathematics or others knowledge areas.

We also give information about databases of investigation articles, different guides of LaTeX and related tools. Finally, we make a general overview of the good and not so good stuff of doing a Ph. D. in Mathematics.

For students' sake, we have done a document in Basque and Spanish where it appears all the information presented in this talk. The document is in the following link: <https://sites.google.com/site/victormmanero/the-beauty-of-math>

# Stochastic Programming and Risk Modeling

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Laureano F. Escudero<sup>2</sup>, Celeste Pizarro<sup>2</sup>, and Giorgio Consigli<sup>3</sup>  
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KEY WORDS: stochastic programming, risk modeling, corporate bond portfolio management.

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Uncertainty is the key ingredient in many decision problems and over the past thirty years different approaches to optimization under uncertainty have been developed. Stochastic Optimization (SO) is a field of Operations Research (OR) that appeared as a response to the need to incorporate uncertainty into mathematical optimization models and it is broadly applied in today real-world applications.

For instance, SO is a very useful tool in the field of finance. Almost all the decisions have to be made taking into account uncertain parameters, sometimes according to several sources of uncertainty. That is the case of the problem we analyze in this work. In addition, in many fields, such as finance, the decisions are made in a risky environment, which has to be modeled. Finding appropriate risk averse measures for each problem is a very important task and it has been widely studied in the literature.

In this work we analyze both, stochastic programming and risk modeling techniques, to solve a corporate bond portfolio management problem.

## CORPORATE BOND PORTFOLIO MANAGEMENT

The 2008 credit crisis has deeply affected the price of corporate liabilities in both equity and fixed income secondary markets leading to unprecedented portfolio losses by financial investors. A coordinated intervention by monetary institutions limited the systemic consequences of the crisis, without, however, avoiding a significant fall of corporate bond prices across international markets. In this work, we analyze alternative portfolio optimization approaches in the fixed income market over a time in which credit derivative markets became very illiquid. All policies are analyzed relying on a unique set of market and credit scenarios generated by common and idiosyncratic risk factors on an extended investment universe.

We also study different approaches for risk modeling, such as, Mean-Risk (MR), Value-at-Risk (VaR), Conditional Value-at-Risk (CVaR), and the new measure Stochastic Dominance Constraints (SDC) introduced by our group as a multistage time consistency extension for the two stage- mixed 0-1 first- order and continuous second-order SDC recently appeared in the literature.

When using these models to study real markets and decision making, some computational needs afloat:

- Those approaches that imply 0-1 variables, become quite non-treatable when considering a big number of scenarios. We are planning to solve them by using the decomposition Branch-and-Fix Coordination (BFC) developed by our group.
- Both VaR and SDC require scenario cross constraints and, then, the related decomposition algorithm development is enormously difficult. “The decomposition BFC-SDC algorithm could be very helpful for these models.
- Time is often a big issue. Sometimes a quick answer is preferable rather than an accurate one. Relaxations such as the Cluster Lagrangian Decomposition (CLD) algorithm developed by our group and the metaheuristic Fix-and-Relax Coordination algorithm (FRCA) developed by our group for providing (hopefully, good) feasible solutions for large-scale stochastic mixed 0-1 problems, additionally providing the quasi-optimality bound of the solution.
- Parallel computing is also a good way to provide better computational times by taking advantage of computers with multicore processors.

# Development of statistical methodology for research: categorization of continuous variables in prediction models

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KEY WORDS: categorisation, cut points, prediction.

Prediction models are currently relevant in a number of fields, including medicine. Decisions such as the most appropriate treatment for a disease, or whether or not a given patient should be discharged, etc., are based on the individual patient's risk of suffering some unfavourable event, and such a risk is often measured on the basis of clinical predictors that are continuous in nature. From a statistical point of view, categorising continuous predictors is not recommended, since it may entail a loss of information and power. However in clinical research and, more specifically, in the development of prediction models for use in clinical practice, clinicians call for the categorisation of continuous parameters. An important reason for this is that decisions in clinical practice are often taken on the basis of an individual patient's risk level, which can be seen as a categorisation of that patient's clinical parameters. Previous work on categorisation of continuous predictors has been done, but almost look for a single cut point. In contrast, we are of the opinion that more than two categories are needed so as to minimise the loss of information with respect to the original continuous variable. Hence, the goal of this research is to develop statistical methodology which allows to select the optimal number and location of cut points to categorise continuous predictors. We considered the particular case in which the response variable is dichotomous, principally because this is one of the most common distributions for outcome variables in clinical prognostic research. Hence, the prediction model selected was the logistic regression model.

We propose two different methodologies for the categorisation of continuous variables. The first one is based on the graphical display of the relationship between the predictor and the outcome while the second obtains the cut points in such a way that the prediction model's discrimination ability is maximised.

## **Categorisation with Generalized Additive Models with p-Splines**

We propose a categorisation methodology, using Generalised Additive Models (GAMs) with P-spline smoothers to determine the relationship between the continuous predictor and the outcome. The proposed method consists of creating at least one average-risk category along with high- and low-risk categories based on the GAM smooth function.

## **Categorization by maximising the area under the ROC curve (AUC)**

We have proposed two methods, named AddFor and Genetic, which consists on categorising a continuous predictor in such a way that the best predictive logistic model is obtained (highest area under the receiver operating characteristic curve - AUC) for the response variable. The AddFor method looks sequentially for the cut points while the Genetic uses genetic algorithms to select the optimal vector of the cut points. The proposed methods have been compared and validated by means of simulations. Additionally, we have developed an R package, named CatPredi, which implements these methods and provides the user with the optimal cut points and the categorised variable to be used in the prediction model.

The above presented approaches have been applied to a prospective cohort of patients with exacerbated chronic obstructive pulmonary disease. Several predictors such as the respiratory rate or the partial pressure of carbon dioxide in blood (pCO<sub>2</sub>) were categorised and the categorical versions performed as successfully as the original continuous variable.

# Adaptive Finite Element Methods with electromagnetic applications

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KEY WORDS: Finite Element Method, Inverse Problems, Magnetotelluric Problem.

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We simulate a variety of electromagnetic applications by solving Maxwell's equation using a highly-accurate self-adaptive Finite Element Method. This method performs local refinements in the mesh until the relative error in the quantity of interest (for instance the electric or magnetic field) decreases sufficiently. This type of adaptive strategy delivers exponential convergence rates, which is the fastest possible type of convergence. In particular, we solve the magnetotelluric inverse problem, a passive electromagnetic exploration technique intended to estimate the resistivity distribution in the subsurface. First, we simulate the magnetotelluric measurements solving Maxwell's equations properly. With them, and solving the inverse problem, we are able to properly invert the simulated measurements in order to recover the subsurface resistivity distribution, and hence, to determine the materials of the formation.

# Modeling and optimization of wireless downlink data networks

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KEY WORDS: Markov Decision Processes, Stochastic Optimization, Scheduling.

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In this work we develop a modeling framework for optimizing the performance of a wireless downlink data network. This model considers a base station, which is transmitting data to certain devices. Due to fading and interferences, the connection between the base station and the devices varies over time. The base station is not allowed to serve more than one device at the same time, and therefore, at any time it has to choose among one of the devices. How to find the right sequence with the goal of minimizing the mean delay of the users in the system is still an unsolved problem.

Our model is based on the multi armed restless bandit framework. This framework allows us to obtain a heuristic policy, which turns out to be opportunistic (a family of schedulers that usually show a good performance). This policy exhibits a great performance in numerical experiments, improving the results obtained by any other scheduler known in the literature. Not only it seems to minimize the mean delay experienced by the users, but it also seems to achieve the maximum stability.

Using fluid limit techniques, and based on our model, we are able to characterize the family of policies that are maximum stable. We also give the sufficient and necessary conditions for a policy to be asymptotically optimal. The heuristic policy described above belongs to the family of maximum stable and asymptotically optimal schedulers, being the only one in the literature with these properties.

# Numerical Bifurcation Analysis of PSPM.

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KEY WORDS: structured populations, delay differential equations, Volterra functional equations, equilibrium, bifurcations, numerical methods.

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Physiologically structured population models are used in biology and ecology to study, from a mathematical point of view, the behaviour of populations, in which the individuals differ due to physiological characteristic, and the interactions of the populations with the environment. The models can be defined in terms of Delay Differential Equations and Volterra Functional equations. Due to the complexity of the models, it is not possible to handle the problem analytically, and so it is necessary to use numerical methods, even to obtain steady states solutions. We present the formulation for a general type of models, and numerical methods to compute equilibrium branches and bifurcation curves under one and two parameter variations. Using this type of formulation and the algorithms proposed, it is possible to obtain biological conclusions for different type of models, including consumer-resource, three trophic, or cannibalistic models.

# Aeroacoustic Simulation of Turbomachinery

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KEY WORDS: Computational Fluid Dynamics, Aeroacoustics, turbo-machinery

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Industry's interest in applying numerical methods to simulate engineering applications has sustained a phenomenal growth recently. Testing has become more closely coordinated with numerical simulations in order to reduce cost,

better understand physical phenomena and save time in bringing products to market. In addition, the advent of affordable high-performance computing, such as commodity clusters and computer capabilities along with the improvement of the underlying numerical methods and visualization tools has widely opened the door to large-scale applications. Computation Aeroacoustics (CAA) which origin backs to 1950's, lately received a big interest by

scientists because of its substantial industrial applications in many industrial sectors such as aerospace, automotive and ventilation. Due to noise harm, stricter standards for noise levels will be required for the next coming years, therefore this important issue should be taken into account in the design process by the industry. Aeroacoustics noise prediction and propagation is a very hard task to achieve, many models and strategies are proposed in the literature but still facing big and very challenging problems. Among others, nonlinearity capturing

fails because of the use of linearized models too close to the near-field due to computational cost-effectiveness limitations. Nonlinearity of noise propagation, which in many situations is very important and could not be neglected, as is the case of high speed turbo-machinery. The objective of the project is to develop cost-effective noise prediction and propagation model base on the Homogenization techniques and semi-analytic approaches that

consider nonlinearity up to the mid-field. This work is part of the BCAM-BALTOGAR project on building an integrated CFD platform for simulation and optimal design using the state of the art of CFD, High performance computing paradigm (MPI) and innovative methods that brings the platform to meet the need of industry in terms

# Optimising the manufacture of offshore mooring chains in Vicinay Cadenas

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KEY WORDS: Flash Butt Welding, Mooring Chains, Optimization.

Vicinay Cadenas S.A. (VCSA) is a steel processing company that specialises in the manufacture of chains and accessories for mooring lines used in the offshore industry, mainly for oil and gas. Its main customers are major oil companies such as Exxon, Shell and BP, which require mooring systems for their offshore rigs. VCSA makes chains of various types to order for its customers, and is a world leader in its field.

Welding is a key part of chain manufacturing. This study seeks to determine how the manufacturing parameters of welding machines influence the appearance of inhomogeneities. The idea is to optimise current manufacturing processes and acquire knowledge that will enable the firm to develop new products with diameters in excess of those produced to date. To that end, multivariate analysis techniques are used to study manufacturing data on various chains and an algorithm is designed that selects the spreads of the adjustable variables that contain the lowest (highest) percentage of links with inhomogeneities.

	Full range	Best spreads
Variable $x_1$	773.14 - 878.32	804.800 - 852.210
Variable $x_2$	163.303 - 172.157	166.920 - 172.050
Variable $x_3$	40.045 - 43.14	40.81 - 42.75
Variable $x_4$	15.162 - 20.558	15.65 - 18.03
Variable $x_5$	44.798 - 47.95	44.800 - 47.040
Variable $x_6$	0.807 - 0.944	0.862 - 0.944
Variable $x_7$	172.578 - 186.032	178.82 - 186.030
N° of links	8.855	1.000

Manufacturing run "B". Full range of the adjustable variables and spreads of those variables containing 1000 links and the lowest concentration of inhomogeneities

The method designed for locating the best and worst spreads of the welding variables was then applied to nine manufacturing runs of chains with different diameters on the same machine, with a view to drawing up a table of settings for it. The results show that the nominal figures for the variables increase when the diameter of the links to be welded increases, in a way that is consistent with the experience of the company. This has led to a modification of the whole table of settings for the machine. The new table is an improvement on the one currently in use at Vicinay Cadenas S.A. The results also provide an estimate for the table or settings that needs to be applied to tackle the manufacture of new, larger chains.



Kimika



Química

# Base-Promoted C→N Acyl Transfer Reaction and Its Application to the Synthesis of A Second Generation Hepatitis C Virus Inhibitor by Enantioselective 1,3-Dipolar Cycloaddition

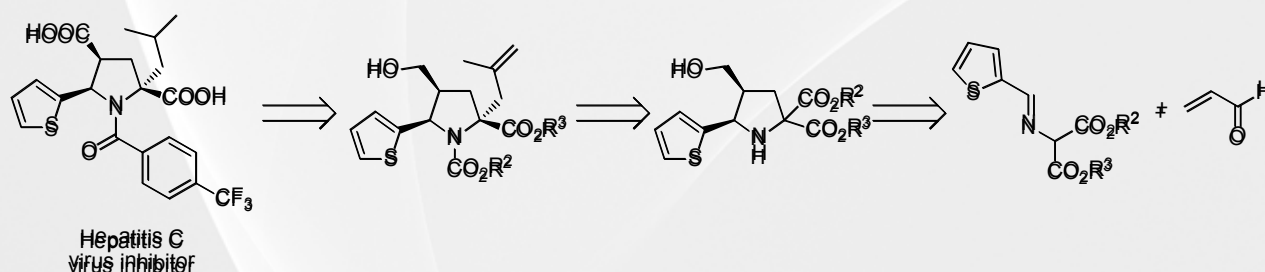
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KEY WORDS: Acyl transfer, Amino acids, Tandem reactions, Hepatitis C Virus Inhibitor.

Hepatitis C virus (HCV) infection is a global health problem that impacts approximately 180 million individuals.<sup>1</sup> HCV, a small, single-stranded positive-sense RNA virus, is a member of the *Flaviviridae* family of viruses that includes other flaviviruses such as bovine viral diarrhea virus, dengue virus, and West Nile virus and is the only member of the genus *Hepacivirus*. At the moment, there are many drugs under clinical trial evaluation, the compounds targeting HCV replication being the most promising candidates to achieve a sustained virological response.<sup>1, 2</sup>

Seeing the importance of these molecules, we developed in our group the synthesis of the second generation antiviral drugs. Firstly a catalytic enantioselective [3+2] cycloaddition reaction between an azomethine ylide and acrolein was carried out,<sup>3</sup> and secondly, we have established a good approach to a diastereoselective decarboxylative protonation process, developing a novel base-promoted rearrangement reaction that converts *N*-substituted  $\alpha$ -aminomalonates into *N*-alkoxycarbonyl  $\alpha$ -amino acid derivatives under mild conditions.



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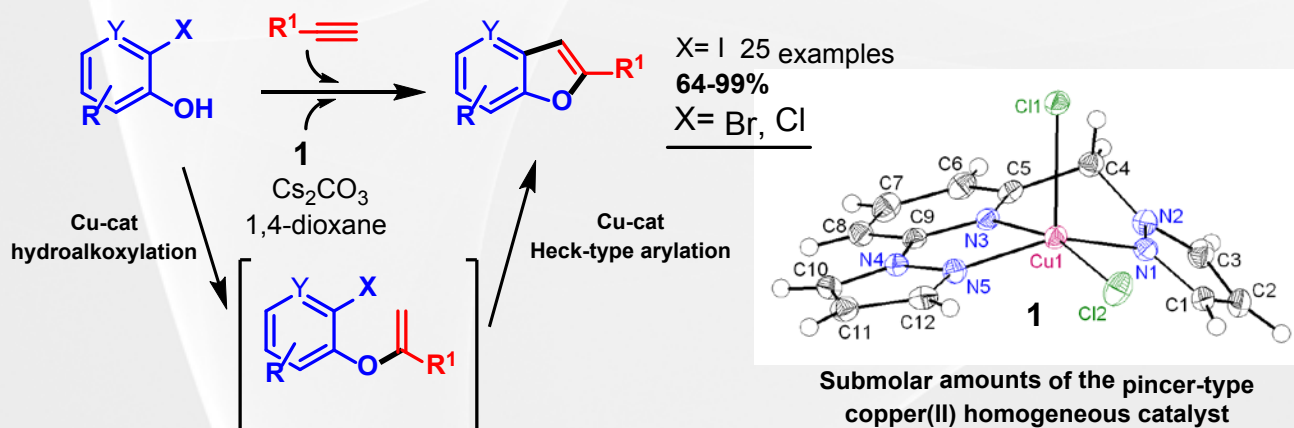
# New strategies for the access to benzo[b]furans.

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KEY WORDS: benzo[b]furans, copper catalysts, hydrophenoxylation

Heteroannulation mechanism demystified. A new non-symmetric Cu (II) pincer complex catalyzes much more efficiently benzofuran formation by reaction between *o*-iodophenols and alkynes. Bromo- and chlorophenols are for the first time heteroannulated. Strong evidences for hydroalkoxylation and Heck-type arylation steps catalyzed by this remarkably active, recyclable homogeneous catalyst are provided.



# Intramolecular Palladium Catalyzed Reactions in the Synthesis of Heterocycles

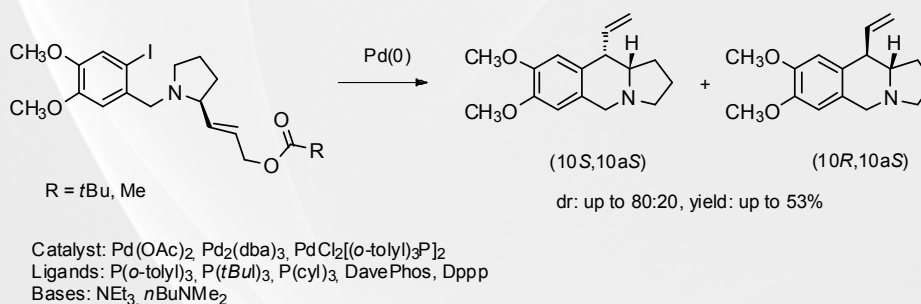
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KEY WORDS: organometallics, palladium-catalyzed cross coupling reactions, heterocycles

The Parham cyclization with alkenes as internal electrophiles may be considered as an intramolecular carbolithiation reaction of unsaturated aryllithiums, which is particularly well suited for the synthesis of functionalized five-member carbocyclic and heterocyclic systems. We have shown that the intramolecular carbolithiation can also be used for the construction of medium size rings, even in a diastereoselective or enantioselective fashion. Up to two contiguous stereogenic centers may be generated, that may be controlled by using chiral bidentate ligands, such as (-)-sparteine, for lithium, which would promote face selectivity on the double bond.<sup>1</sup> We have also investigated the Mizoroki-Heck (M-H) reaction as an alternative strategy for the carbolithiation reactions, since the same substrates can be used in both types of intramolecular reactions. In this context, we have demonstrated that the intramolecular palladium-catalyzed reaction of 2-alkenyl substituted *N*-(*o*-iodophenylalkyl)pyrroles can be switched from alkene (M-H reaction) to pyrrole nucleus (C-H functionalization) by choosing the adequate catalytic system.<sup>2</sup>

We have also study the possibility of generating a quaternary centre on the pyrroloisoquinoline skeleton using an asymmetric Mizoroki-Heck cyclization, as well as asymmetric palladium-catalyzed polyene cyclization. On the other hand, we have also studied the generation of tertiary centres using the corresponding 2-alkenyl substituted *N*-(*o*-iodophenylalkyl)pyrrolidines with a good leaving group in the alkene to carry out a  $S_N2'$  process. In this case, the reaction has been carried out in a diastereoselective fashion starting from chiral substrates. Different catalytic systems and experimental conditions have been tried to control the stereoselective of these reactions, but with moderate success till now.



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# Piezoelectric polyimides for high temperature applications

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KEY WORDS: piezoelectric, polyimides, sensor.

The use of polymeric materials for sensor applications has a great interest, because their chemical and physical properties may be tailored over a wide range of characteristics. The field of piezoelectric polymers has long been dominated by ferroelectric polymers from the polyvinylidene fluoride (PVDF) family. The piezoelectricity in this polymer class arises from the strong molecular dipoles with the polymer chain and from the resulting change of the dipole density upon application of a mechanical stimulus. This semi-crystalline polymer show a complex structure and can present five distinct crystalline phases related to different chain conformations, although only the  $\beta$  phase has interest. In addition, this ferroelectric polymer shows a relatively low thermal stability of the piezoelectric effect, limited to below 100°C. Therefore, there was a large interest in synthesizing new piezoelectric polymers for high-temperature applications.

Among various amorphous piezoelectric polymers, aromatic polyimides with a high dipole moment in the repetitive units (cyano groups, -CN) were chosen, because their excellent thermal, chemical and electrical properties.

Our research elapses along all the research stages, from the monomer synthesis to the polymers characterization. For example, the synthesis of the monomer with two cyano groups (diamine 2CN) is made by aromatic nucleophile substitution (SNAr) in a two-step reaction.

Polyimides were obtained by reaction between the dianhydride 4,4'-oxydiphthalic anhydride (ODPA) and a diamine in a two-step reaction. In the first step, a nucleophilic attack of amine groups toward carbonyl groups in the dianhydride produces the poly(amic acid); in the second step, the cyclodehydration reaction caused by thermal treatment gives rise to the polyimide.

Once the polyimide film is obtained, the sample poling is performed. Poling is the process of generating net remnant polarization in the material by applying sufficiently high electric field at a temperature higher than its glass transition temperature, in order to get most of the molecular dipoles oriented in the same direction. This electric field can be applied by two different ways, which they are called corona poling and contact poling.

After completing the polymeric material preparation, the material characterization is conducted. Apart from the general characterization made for a common polymer such as, Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR), Gel Permeation Chromatography (GPC), Differential Scanning Calorimetry (DSC) or Thermogravimetric Analysis (TGA), specific studies are needed. For example it is measured the Piezoelectric Charge Constant ( $d_{33}$ ) and the dielectric properties (dielectric permittivity and dipole relaxations) are studied by dielectric spectroscopy and Thermally Stimulated Discharge Current (TSDC)

# The Uncommon Three-Ring Structure of Scopoline Revealed from Gas-Phase Isomerization of Scopoline

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KEY WORDS: alkaloids, rotational spectroscopy, supersonic jet.

Tropane alkaloids have diverse pharmacological uses and are well-known for their neurostimulant activity. Previous structure-activity-relationship established correlations between bioactivity and several aspects of ligand conformation and stereochemistry, including delicate intramolecular effects like nitrogen inversion. We have initiated a series of structural studies on tropane alkaloids, aimed to discerning their intrinsic stereochemical properties using rotational spectroscopy in supersonic jets. Here we extend these studies to the epoxytropanes, initially motivated to interrogate the influence of the epoxy group on nitrogen inversion and ring conformation. The rotational spectrum evidences a single structure in the gas phase, providing a first description of the (three ring) structurally-distorted tropane in scopoline. The determined rotational parameters of scopoline reveal the structural consequences of the intramolecular cyclation of scopoline, which breaks the original epoxy group and creates a new ether bridge and a 7 $\beta$ -hydroxytropane configuration. The hydroxyl group further stabilizes the molecule by an O–H  $\cdots$  N intramolecular hydrogen bond, which, in turn, forces the N-methyl group to the less stable axial form b. The experimental work was supported by ab initio and DFT calculations.

# Ultrafast Photophysics of Pyrrole

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KEY WORDS: chromophore, dark state, femtosecond spectroscopy.

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Simple aromatic molecules as pyrrole, indole or phenol, which are characterized by having bright  $\pi\pi^*$  electronic transitions, appear as chromophoric units of many relevant biological species. Often their photophysical properties are strongly dependent on the interaction of these  $\pi\pi^*$  excitations with dark  $\pi\sigma^*$  type states with repulsive character along some vibrational coordinates. The interplay between these two types of states triggers a complex dynamics that takes place in the femto-picoseconds scale.

Herein, we present a time domain study on the relaxation dynamics of isolated pyrrole after excitation in the 265-217 nm range, by applying femtosecond time delayed ionization. The work provides a comprehensive view of the photophysics of the molecule, which is determined by the  $\pi\sigma^*$  character of its lowest electronic excited state. The study also explores the influence on the transient signals of intermediate resonances met during the probing process, substantiating the importance of a correct choice of the zero delay-time reference.

# Optimization of supercritical fluid successive extractions of fatty acids and polyphenols from *vitis vinifera* grape wastes

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KEY WORDS: fatty acids, polyphenols, supercritical fluid extraction, optimization.

Due to the fast pace of life that we live in, during last decades, there have been changes in the alimentation habits and in consequence also in the food that we consume. Thus, the food processed industrially has turned into something indispensable into our daily life, and, of the same way, the supplements have turned also in necessary to compensate the loss of the nutritional value. Polyphenols and the fatty acids are among them.

On the one hand, due to their antioxidant capacity, polyphenols can neutralize free radicals turning them in less dangerous thereby stopping side reactions. This ability makes them interesting for many different applications such as for the treatment of inflammations or human degenerative diseases as cancer, for anti-ageing aims in cosmetics or for nutraceutical purposes as to reduce food product deterioration. Moreover, polyphenols are known to be nootropics, owing to be helpful in several functions of the brain; such as learning, memory, attention or motivation. On the other hand, polysaturated fatty acids play an important role in cardiovascular prevention and monosaturated fatty acids reduce blood total triacylglycerol and cholesterol levels, in this way it plays an important role in cancer prevention.

Fatty acids and polyphenols were extracted successively from wine wastes (two different *vitis vinifera* grapes) with very good yields, using previously optimized Supercritical Fluid Extraction (SFE) method. The method consisted in two steps. In the first step fatty acids were extracted without extracting polyphenols and in the second step polyphenols were extracted without fatty acids. The two steps were optimized individually analyzing four parameters by means of a Central Composite Design (CCD). The parameters were temperature, flow, pressure and time of extraction in the fatty acids extraction (first step) and temperature, flow, pressure and percentage of methanol as modifier in the polyphenols extraction (second step). Concerning quantification, fatty acids were determined by means of Gas Chromatography coupled to Mass Spectrometry (GC-MS) after a derivatization step, and the polyphenols with High Performance Liquid Chromatography coupled to Tandem Mass Spectrometry (HPLC-MS/MS) and the Folin-Ciocalteu method. Optimal SFE conditions were identified as 5 minutes, 35 °C temperature, 250 bar pressure and 2 mL/min flow in the first step for fatty acids, and 45 °C temperature, 140 bar pressure, 1.75 mL/min flow and 40 % methanol as modifier in the second step for polyphenols.

In this work has been achieved for the first time, as far as we know, a SFE method for the successive extraction of fatty acids and polyphenols from the same wine wastes with very good yields. This method appears to be a promising alternative for a full revalorization of wine wastes before giving it any other application. The optimized method was successfully applied to two samples obtaining very good yields. The results of the white grape residues are particularly promising; however it would be interesting to carry out a study with more grape varieties to reach more accurate conclusions.



# Hazardous Pollutants: from the Soil to Living Organisms. Health Risk Assessment due to the Weathering Processes of Metal(loid)s.

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KEY WORDS: mining activities, chemical hazard, green chemistry.

The combination of rich mining ores with the proximity to the sea converted the Basque Country in a very favourable place for mining already in Roman times. However, the production of minerals for economic use involves a series of physical and chemical processes that may easily pose a relevant hazard. Thus, the main objectives of the thesis can be summarized into: characterization, risk assessment (mainly for human beings) and cleanup proposal of abandoned mining areas.

Knowledge of the operating history of the site will be valuable during site scoping, site characterization and the cleanup alternative selection process. Nonetheless, this background information provides valuable insight into the contaminants that may be present, potential threats to human health and the environment, the feasibility of response actions, as assisting in the location of potential physical hazards (abandoned structures).

## CHARACTERIZATION

The characterization has been developed in the Department of Analytical Chemistry as a resource for public interest groups, local inhabitants and project managers, among others, that are working on addressing the environmental concerns posed by inactive mines and mineral processing sites.

As an attempt to look for a greener chemistry, the destructive techniques (ICP-MS, etc.) commonly used to achieve that goal were combined -when not completely replaced- by direct and non-destructive spectroscopic tools (Raman spectroscopy, SEM-EDX, SCA) that together with chemical simulation programs give new insight into the information obtained.

## RISK ASSESSMENT

While the majority of inactive mine sites are not believed to present significant environmental problems, there are, nonetheless, many sites that do create significant impacts. Among the affections studied here that require remediation and ultimately can impact human health there should be highlighted:

- Metal contamination of soils.
- Acid generation, which is one of the largest problems from hard rock metal mining.
- Metal contamination of ground/surface water and sediments.
- Air emission and deposition of metal-rich particulate matter.
- Bioaccumulation of hazardous metals and their introduction into the food-chain.

## CLEANUP

Often in evaluating cleanup options at mine sites, a watershed approach to assessing environmental impacts will be required to understand the scope of potential problems and design appropriate solutions. Partnerships can facilitate the design of cleanup strategies that address multiple interests within a watershed. Collaborative efforts to set priorities for mine site characterization and cleanup, coupled with utilization of the appropriate mix of regulatory and non-regulatory tools for getting the work done should result in successful projects.

# Metabolomics applied to organ maturation studies in paediatric population

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KEY WORDS: metabolomics, neonates, steroids, LC-MS

One of the most significant problems that are faced in paediatrics is the lack of authorized drugs for its use in children. This is due to the scarcity of clinical trials approved for under-aged patients. As a result, it is common the use of drugs without specific indication for this population and therefore without a well-established posology. Commonly, the dosage is extrapolated from the adult dosage regimen by correlation with the body weight or the superficial area, assuming this as a linear correlation. However, considering the incomplete maturation of the organs involved in the ADME processes of the drug in children, this linearity can be estimated as erroneous, leading to incorrect dosing. For this reason the objective of this work is the use of targeted and untargeted metabolomics to search for biomarkers correlated with the state of maturation of the organs involved in drug elimination in animal models of paediatric population.

Steroids are studied as possible biomarkers for maturation of organs by targeted metabolomics. Steroids play a fundamental role in a wide variety of physiological functions: are involved in the regulation of sexual differentiation, take part in the development of secondary sexual characteristics, are implicated in electrolytic regulation, and are crucial in numerous enzymatic reactions among other functions. Nevertheless, steroid concentration levels vary along the human being life, not only as a result of pathologies such as congenital adrenal hyperplasia or Cushing syndrome, but also because of the regular development of the body, particularly during the childhood, adolescence and pregnancy. In addition to this, steroids share metabolic pathways with the elimination of some drugs prescribed in paediatrics, so that the analysis of these endogenous compounds could be useful in the prediction of the drug behaviour in the patient.

Pigs were chosen as animal models because of the similitude of their metabolism with the human. The equivalent of the childhood in human (up to twelve years) is fourteen weeks for pigs. For this purpose an analytical method based on LC-MS/MS is developed for the simultaneous determination of eleven steroids: aldosterone, cortisol, corticosterone, Reichstein's Substance S, testosterone, deoxycorticosterone, androstenedione, 17 $\alpha$ -hydroxiprogesterone, dihydrotestosterone, progesterone and pregnenolone. Different sample treatments were studied. A simple protein precipitation with a preconcentration step was the most adequate treatment for plasma samples.

Real pig plasma samples were analysed with the optimized treatment and LC-MS method. Cortisol was the only steroid with concentration levels over the limits of detection of the analytical method. The future of the research addresses to improve sensitivity by means of derivatization or by using high resolution mass spectrometry equipments, more sensible than the already used.

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# Electrodes for electrical double-layer capacitors

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KEY WORDS: nanocarbon, graphene, supercapacitors

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Double-layer capacitors or supercapacitors provide a complementary mode of electrical charge and energy delivery to batteries. The amount of charge stored, and eventually released, per unit of voltage in the electric field of the electrical double-layer will depend on the surface area and pore dimensions of the electrode materials, these materials are usually activated carbons with surface areas  $\sim 1000 \text{ m}^2.\text{g}^{-1}$ .

## NANOPOROUS CARBONS FROM LIGNIN

Microporous lignin-derived carbons with surface areas ranging between 800 and 1300  $\text{m}^2.\text{g}^{-1}$  and narrow and tuneable pore size have been produced by activation with KOH at 900 °C. Results for different content of KOH relative to carbon, suggest that the pore size ( $\approx 1 \text{ nm}$ ) and specific surface area are highly influenced by the crystal size and defect concentration of graphene layer. The relation between microtexture and microstructure also reveals the competition between the oxidation reaction of carbon by KOH and the intriguing C–C re-organization provoked by chemical activation.

Results related to material properties of the most adapted pore size and to the electrolyte characteristics and their effect on its capacitive properties in symmetric double-layer capacitors were assessed. Gravimetric capacitance up to 89  $\text{F}.\text{g}^{-1}$  was obtained in an organic electrolyte while 104  $\text{F}.\text{g}^{-1}$  were achieved in an ionic liquid.

## GRAPHENE-BASED ELECTRODES

Graphene, a one-carbon atom thick material with a theoretical surface-area  $> 3000 \text{ m}^2.\text{g}^{-1}$ , has been proposed as a competitive electrode material for supercapacitors because of its adaptive porous structure, low ion transport resistance and chemical tunability, among other reasons.

Graphene-based materials have been prepared and then integrated in electrodes for supercapacitors. These materials are being studied by nitrogen gas adsorption/desorption, X-Ray diffraction, Raman spectroscopy and Scanning and Transmission Electron Microscopy, among others. Then, the graphene-based electrodes have been characterized by using electrochemistry techniques like cyclic voltammetry, galvanostatic charge/discharge cycling and impedance spectroscopy of the supercapacitor cells in a 3- and 2-electrode configuration.

# Photoactive Hybrid Materials for Technological and Biomedical Applications

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KEY WORDS: Laser Dyes, Zeolite, AlPOs, Metal Organic Framework, Atomistic Simulation, Photosensitizers, Nanoparticles, Photodynamic Therapy

The encapsulation of photoactive molecules in different hosts results in composite materials with interesting promising applications in many technological and biomedical fields. The solid framework offers a rigid and robust environment for fluorescent molecules improving their emission capacity and thermal stability and infers a high organization degree. In this sense, the photophysical characterization of the dyes and dye-doped materials is a key factor to understand the involved processes or to develop new dyes with tailor-made physicochemical properties. Accordingly, quantum mechanical simulations have become a powerful tool to complement the experimental work and orient future strategies.

Here, we present the main research lines in the Molecular Spectroscopy Group divided in five main lines:

1. **BODIPY dyes.** Their photophysical properties can be controlled by the substitution pattern. Our interest in this field is focused on the spanning of their fluorescence and lasing region to the blue as well as to the red part of the visible. Furthermore, their chemical stability allows their use as sensors to monitor the environment characteristics or detect the presence of an analyte.
2. **Dyes doped 1D-nanostructures.** The encapsulation of guest fluorophores into the unidimensional pores of zeolite L and AlPOs leads to photoactive materials with interesting properties for applications such as antenna and white-light emitting devices, non-linear optics, colour switching, etc.
3. **Metal-organic frameworks (MOFs).** The design of a PCP with photoactive entities as part of the structure or confined in the pore as guests can contribute to the development of multiple applications such as molecular sensors, materials for laser, NLO properties, etc.
4. **Dyes doped nanoparticles.** By encapsulating two dyes (Rhodamine 6G and Nile Blue) with appropriate spectral overlap to give rise to an Energy Transfer process (FRET) into latex nanoparticles, a highly efficient and stable emission in the red region of the visible has been reached with applications for lasers in biomedicine. Furthermore, by the incorporation of photosensitizers into silica nanoparticles (embedded in or covalently anchored on the outer surface) a hybrid system with potential application in photodynamic therapy of cancer is desired.
5. **Atomistic simulation.** The above described systems are also studied by atomic scale simulations. We aim to complement experimental observations and help to understand the effect of confinement on the guest molecule's photophysics.

To perform all the studies, the laboratory is equipped with spectroscopic (absorption, and steady-state and time-correlated fluorescence) techniques and different fluorescence microscopies. Photophysical characterization is not only performed in solution but also in solid state or suspension (polymers, clays, zeolites and aluminophosphates). The obtained materials are being successfully applied in dye lasers, sensors, white light emitters and antenna devices, as result as of the consolidated collaborations established by the group in the last years.

# Ingeniaritza kimikoa eta kimika

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Ingeniería Química  
y Química

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# Microencapsulation and microwave drying technologies to obtain enriched food material

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KEY WORDS: microencapsulation, drying, microwave, food additives.

Nowadays, there is a growing interest in food additives, such as vitamins, antioxidants or probiotics, which are added to enrich nutritionally habitually consumed foods (bread, pasta...). In order to reach this goal, microencapsulation techniques are used for protecting the substances to be added. When the substances are microencapsulated, a technology of a microwave drying on a fixed-fluidized is proposed in order to dehydrate thermosensitive materials, allowing a less deterioration, mayor stability and an increase of the lifespan.

Microcapsules are made with 2% of alginate and coated with chitosan, using an extrusion technique called *Jet Cutter*, obtaining spherical microcapsules of about 500  $\mu\text{m}$  diameter. The microcapsules were dehydrated in a microwave drier that consisted of the following essential elements: an air dryer, a heating and cooling air and optical fibers to follow the temperature. A series of experiments were planned with different phases and temperature levels. As consequence of the microwave experiments the most adequate operating conditions could be established. Some of significant benefits derived of microwave drying are as follows:

1. Opposed to the traditional drying in this case, the microwave dehydration takes place from the heat released inside of material due to the water content.
2. An inverse temperature gradient appears favoring moisture removing and promoting the drying of the microcapsules.
3. Compared to conventional systems, the temperature level and the processing times are reduced.

Combination of microencapsulation and microwave drying seems to be a very promising method to obtain enriched foods. From the results of this research the following general conclusions have been obtained:

- The *Jet Cutter* microencapsulation technology enables less deterioration of the encapsulated substance.
- Microwave drying in fixed-fluidized bed gives us a good temperature control and a better product quality over conventional drying.
- In the drying process, three phase characteristics are observed: Phase I is characterized by the removal of surface moisture, in Phase II the diffusional control appears because the water has to emerge from the inside of the material and finally the phase III, which is the final drying stage for removing the remaining moisture.
- This technology reduces drying times easily, reaching the level of moisture content required for product quality control and non-proliferation of microorganisms.
- It is necessary to search for appropriate measures to minimize the deterioration of the heat-sensitive compounds and to enable the kinetics of the process operational strategies.
- Reducing processing times also reduces the energy consumption (cost of the process), which may sometimes be subjected to the quality of dehydration.

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# Deactivation of HZSM-5 Zeolites Catalysts in Sustainable Refinery processes

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KEY WORDS: Petrochemicals, Fuels, Bio-Oil, HDPE, Coke deactivation, Spectroscopic characterization.

## THE PROBLEM OF CATALYST DEACTIVATION

The chemical industry needs to gradually shift the raw materials from fossil to sustainable sources. Thus, the “Sustainable Refinery” concept appears to include several concepts: Bio-Refinery, use of renewable raw materials such as biomass and CO<sub>2</sub>; Waste refinery, use of municipal waste as plastics and tires; Renewed conventional refinery, to enhance the recovery of all petroleum residues.

In the catalytic transformation processes of the Sustainable Refinery, the deactivation is a very important factor: it determines the selection of the catalyst, the reactor design, the operation strategy and the viability of large-scale catalytic processes. For this reason is necessary to minimize the problem, which requires a deeper knowledge of the deactivation mechanisms.

## TOOLS FOR THE STUDY OF DEACTIVATION OF HZSM-5 ZEOLITE

The PROCAT-VARES group studies the deactivation of different types of catalysts: acid, metallic and bifunctional, in order to: i) improve the properties of the catalysts for stability, ii) understanding the mechanisms of deactivation to propose a kinetic realistic mechanism. Among the different catalysts studied, the zeolite HZSM-5 (deactivated by coke deposition) shows an excellent performance in the different processes for the biomass (bio-oil to hydrocarbons) and waste (catalytic pyrolysis of polyolefins) valorization, among others. Therefore in order to promote the technological development of these new processes, the knowledge of deactivation is needed. In order to study the mechanism of coke formation and its relation to the properties of the components of the catalyst and reaction medium is necessary to use a set of different analytical techniques (thermogravimetric, spectroscopic, microscopic...). In this sense, our group is working in the adaptation of these techniques, with the aim of studying the coke and the deactivated catalysts.

## BIO-OIL TO HYDROCARBONS

Our group has been studying valorisation routes for this renewable source of hydrocarbons for more than a decade, and among these routes; the transformation of bio-oil on HZSM-5 zeolite yields selectively C<sub>2</sub>-C<sub>4</sub> olefins and BTX aromatics (benzene, toluene, xylene). At the optimal reaction conditions for obtaining these products, the coke deposited on the catalyst accounts for  $3.02 \cdot 10^{-2} \text{ g}_{\text{coke}}/\text{g}_{\text{catalyst}}$  and consists in condensed polyaromatics with carboxyl, ethers and aliphatic groups. The composition of the coke that deactivated the catalyst has a direct relationship with the concentration of bio-oil components. The results have allowed improving the catalyst properties by generating mesopores in the zeolite and delimitating suitable range of reaction conditions.

## CATALYTIC PYROLYSIS OF POLYOLEFINS

The transformation of high-density polyethylene (HDPE) wastes into C<sub>2</sub>-C<sub>4</sub> olefins (yields higher than 60 wt%) has been performed in the sequential pyrolysis-cracking process: pyrolysis in a conical spouted bed reactor, and cracking in a fixed bed of zeolite catalyst. At the optimal reaction conditions for obtaining these products, the coke deposited on the catalyst accounts for 1.2 wt%  $\text{g}_{\text{coke}}/\text{g}_{\text{catalyst}}$ . There are two types of coke: Coke I has an aliphatic nature and it is localized outside of the zeolite crystals on the mesoporous and macroporous structure, and coke II has an aromatic nature in the exterior of the zeolite pores. The results have allowed establishing a kinetic model that considers the effect the reaction medium components have on coke formation, as well as on the shift in location of the coke from the inside towards the outside of the zeolite crystals.

# Chemical recycling of post-consumer plastic wastes into added-value products (raw materials and fuels)

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KEY WORDS: Chemical recycling, solvolysis, hydrocracking, PET, PU, PS.

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Increased environmental awareness, legislative measures, and public demand for environmental sustainability are leading to a growing interest in plastics recycling. Plastics or polymer recycling is very important for a wide number of reasons such as conservation of oil, reduction of greenhouse gas emissions, saving of landfill space, conservation of energy, and benefits of reuse. Four main approaches have been proposed for plastic waste recycling, namely primary or in-plant recycle of the scrap material of controlled history, secondary or mechanical, tertiary or chemical and quaternary or recovery of energy through incineration. Among these recycling techniques, the only acceptable one according to the principles of sustainable development is the tertiary or chemical recycling since it leads to the formation of the raw materials or monomers and fuels. More particularly our research group is focused on the catalytic solvolysis by hydrolysis or glycolysis (with ethyleneglycol) of post-consumer poly(ethylene terephthalate) and polyurethane, and the thermal and catalytic hydrocracking of polystyrene (HI-PS).

The main objective of the chemical valorisation of complex mixtures of plastic streams is the yield of fuels. A special attention has been paid to developing highly active catalytic systems which combine the bifunctional character given by the metallic sites (platinum) and acidic sites (given by acidic zeolitic supports). In this sense, apart from a suitable surface acidity, the external surface area of the resulting catalyst appears to be of critical importance. A wide variety of zeolites have been explored including different hierarchical and delaminated protonic structures (ZSM-5, beta, ITQ-6 and ferrierite). This type of catalyst (zeolite-supported platinum catalysts) have led to a marked increased in conversion with respect to the thermal process and more importantly, a marked selectivity to a wider and more interesting variety of products in the gasoline range has been achieved.

As for PET recycling both hydrolysis and glycolysis have been investigated as potential routes for waste valorisation. In the case of hydrolysis the use of phosphonium quaternary salts as catalysts in the presence of sodium hydroxide have been explored. Activity levels were high at relatively low temperature (about 100 °C). Furthermore, kinetic correlations provided a reliable mathematical reaction model for this recycling process. However this process may be not appropriate due to the cost and difficult recovery of the quaternary salts and the need of correct management of the residual basic stream. As a viable environmentally-friendly alternative, recycling by glycolysis with ethyleneglycol over sodium carbonate as catalyst has been thoroughly investigated. A good yield of the highly pure monomer bis(2-hydroxyethylene terephthalate) was obtained (80%). The glycolysis process, including the depolymerization reaction and separation for obtaining the highly pure monomer, was designed and optimized in order to increase the global efficiency thereby improving the economical viability of the recycling technology. In order to sustain an economically viable recycling programme, secondary end-use applications of the reclaimed BHET have been developed. Our attention has been focused on the conversion of the purified BHET into unsaturated polyester resins.

More recently, glycolysis has also been selected to depolymerise flexible PU wastes to recover the polyol. Preliminary results on the influence of several factors (namely, temperature, time, the catalyst (NaOH) to solvent (diethyleneglycol, DEG) mass ratio, and the catalyst/solvent to polyurethane mass ratio) on the yield of polyol have been obtained.



# Catalysis for clean energy production: Hydrogen purification

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KEY WORDS: hydrogen production, hydrogen purification, OWGS.

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The increasing economic development in the world has brought an increase in energy consumption, so it is necessary to develop a new energy map where renewable energies would occupy a prominent place to meet the demand and assure the energy supply, protecting the environment. In addition to reducing air pollution and emissions of greenhouse gases, the use of hydrogen as an “energy vector” would reduce the current dependence on fossil fuels, thus promoting the development of fuel cell technology (particularly in the transport sector).

TQSA research group has focused its efforts on the development of catalysts for producing H<sub>2</sub> –rich streams from different types of gas-phase reforming (POX (Partial Oxidation), SR (Steam Reforming), OSR (Oxidative Steam Reforming)– from hydrocarbons of different nature –natural gas (CH<sub>4</sub>), petrol (*i*-C<sub>8</sub>H<sub>18</sub>), diesel (*n*-C<sub>14</sub>H<sub>30</sub>) – Among the catalysts developed for this purpose, NiAl<sub>2</sub>O<sub>4</sub>(Al<sub>2</sub>O<sub>3</sub>), obtained from the nickel aluminate spinel, offers several advantages in reforming processes, such as high catalytic stability and high metal dispersion after reduction at high temperature. These catalysts have been tested in their traditional powder form, but the objective now is to incorporate them in structured metallic wire mesh catalysts, which would allow working at higher space velocity with a minimal pressure drop.

The H<sub>2</sub> produced is then fed to the fuel cell. Since the fuel cell has a low tolerance for CO and its content in the hydrogen stream should be minimized (<1 ppm under stationary conditions and <25 ppm for specific peaks), a prior purification to reduce the content of CO and enrich the H<sub>2</sub> stream is required, first by water gas shift reactions (WGS) and then by CO oxidation (CO-PROX), thus preventing poisoning.

The most viable alternative during the transition to the widespread use of hydrogen in automotive is the on-board production. Therefore, our aim is the *in situ* generation of H<sub>2</sub> and the design of a catalytic converter to perform both the WGS reaction and CO-PROX reaction, i. e. the Oxygen-enhanced WGS (OWGS), in order to purify the hydrogen stream from the hydrocarbon reforming. In this way, the volume of the converter could be reduced, thus making it more viable for its employment in the automotive industry.

Bimetallic Au-Co<sub>3</sub>O<sub>4</sub>/CeO<sub>2</sub> and Au-CuO/CeO<sub>2</sub> catalysts have been synthesized for this OWGS process, achieving higher conversions than those obtained in the WGS reaction. In order to reduce both the cost and the converter size, the catalysts have been incorporated into monolithic structures, which allow working at higher space velocity, thus getting higher conversions than those obtained with the powder catalysts.

# Catalysis for the removal of gaseous pollutants from mobile and stationary sources

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KEY WORDS: Catalysis, mobile sources, stationary sources, NO<sub>x</sub>, Cl-VOC, PCDD, PCDF, methane.

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The work summarized in this contribution is directed to research and development on chemical technologies for cleaning gas effluents by catalytic destruction of the pollutants, mainly centered on those most difficult to eliminate. Research is focused on two main lines with different final application: mobile and stationary sources.

## MOBILE SOURCES

Research in this line is centered on the two main technologies available, at present, for removal of NO<sub>x</sub> present in exhaust gases from automobiles with Diesel engines: NO<sub>x</sub> storage and reduction (NSR), and NO<sub>x</sub> selective catalytic reduction (SCR). NO<sub>x</sub> are particularly difficult to remove from oxidizing exhausts such as those in Diesel vehicles.

The former technology (NSR) requires a catalyst combining sites for NO<sub>x</sub> adsorption, and metallic sites able to favor oxidation and reduction reactions. A model NSR catalyst consists of platinum and barium supported on alumina. During normal operation, oxidizing exhaust gases containing NO<sub>x</sub> pass through the catalytic bed. NO<sub>x</sub> is adsorbed on the catalytic surface until saturation. Then, a reducing agent such as hydrogen is injected for a short time to the gases entering the catalytic bed, and adsorbed NO<sub>x</sub> are desorbed and reduced preferentially to N<sub>2</sub>. The latter technology (SCR) uses zeolitic structures interchanged with metals as catalysts. A model SCR catalyst consists of a Cu-zeolite. During operation, a small amount of NH<sub>3</sub> is mixed with the oxidizing exhaust gases entering the catalytic bed. NH<sub>3</sub> and NO<sub>x</sub> are adsorbed on the catalytic surface, where they react to selectively produce N<sub>2</sub>.

Recently, both technologies have been combined in two catalytic beds arranged in series, NSR-SCR, which allows for virtually zero-emission exhausts.

## STATIONARY SOURCES

Among the wide variety of pollutants in emissions from stationary sources, research in this line is centered on catalytic removal of a single group of pollutants, such as methane or chlorinated volatile organic compounds (Cl-VOC), on the one hand, or the simultaneous removal of several pollutants of different chemical nature present in the same exhaust stream, such as dioxins (PCDD) and furans (PCDF) together with NO<sub>x</sub>, on the other.

Methane is mostly present in emissions from Power plants and Natural Gas engines, Cl-VOC are formed in PVC chemical plants and several industries such as metallurgy, textile or electronics, and their removal requires either high temperatures or very active catalytic formulations. Combined emissions of PCDD/F and NO<sub>x</sub> occur in municipal waste incinerators, for example, where the objective is the removal of all pollutants from the exhaust in a single catalytic stage.

In this line, a wide variety of catalysts has been studied, including Pt or Pd supported on alumina, zeolites, CeO<sub>2</sub> and cerium-zirconium mixed oxides, Mn<sub>2</sub>O<sub>3</sub> and manganese-zirconium mixed oxides, Co<sub>3</sub>O<sub>4</sub>, V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>, etc., always seeking for the best combination of catalytic activity, selectivity and durability for each application.

# Porous M<sup>II</sup>/Pmdc Neutral Frameworks: Synthetic Influence on their CO<sub>2</sub> Capture Capacity and evaluation of CO<sub>2</sub>-Adsorbent Interactions

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KEY WORDS: Metal-Organic Frameworks, X-ray analysis, CO<sub>2</sub> adsorption.

Metal-organic frameworks (MOFs) have recently received significant attention as functional materials because of their various potential applications in catalysis, gas storage, chemical separations, sensing, ion exchange, drug delivery and optics.<sup>[1-2]</sup> It is worth mentioning that their large surface areas, adjustable pore sizes and controllable functionalities are key factors for using MOFs as promising candidates in adsorptive separations and purification purposes.<sup>[3]</sup> In particular, the suitability of the MOFs in CO<sub>2</sub> capture and sequestration (carbon capture and sequestration (CCS)) technologies is remarkable, in which compared with the existing methods thus far, the CO<sub>2</sub> capture by means of adsorption in porous materials presents a higher energetic efficiency.<sup>[4]</sup>

An effective method to achieve that goal is a functionalisation of the pore surface to enhance the affinity towards certain gas molecules, thereby influencing the sorption and selectivity properties.<sup>[5]</sup> In this sense, generation of materials possessing exposed metal-cation sites in the pores (that is, sites that are coordinatively unsaturated after solvent removal so that it permits close approach of guest molecules to the pore surface) has been elected as a very useful strategy of maximising the interaction towards CO<sub>2</sub>.<sup>[6]</sup>

At a first stage, the understanding of the factors that affect the real pore-network structure for a given bulk material due to different synthetic procedures is essential to develop the material with the best adsorption properties. In this work, we have deeply studied the influence of the crystallinity degree over the adsorption capacity on three new isostructural MOFs with the formula  $\{[\text{CdM}(\mu_4\text{-pmdc})_2(\text{H}_2\text{O})_2]\cdot\text{solv}\}_n$  (in which, pmdc=pyrimidine-4,6-dicarboxylate; solv=corresponding solvent; M<sup>II</sup>=Cd (1), Mn (2), Zn (3)).<sup>[7]</sup> Compared with other methods, the solvent-free synthesis stands as the most effective route because, apart from enabling the preparation of the heterometallic compounds **2** and **3**, it also renders the adsorbents with the highest performance, which is indeed close to the expected one derived from Grand Canonical Monte Carlo (GCMC) calculations. The structural analysis of the as-synthesised and evacuated frameworks reveals the existence of a metal atom exposed to the pore. The accessibility of this site is limited due to its atomic environment, which is why it is considered as a pseudo-open metal site. The chemical and physical characterisation confirms that this site can be modified as the metal atom is replaced in compounds **2** and **3**. To assess the effect of the metal replacement on the adsorption behaviour, an exhaustive study of CO<sub>2</sub> experimental isotherms has been performed. The affinity of the pseudo-open metal sites towards CO<sub>2</sub> and the distribution of the preferred adsorption sites are discussed on the basis of DFT and GCMC calculations.

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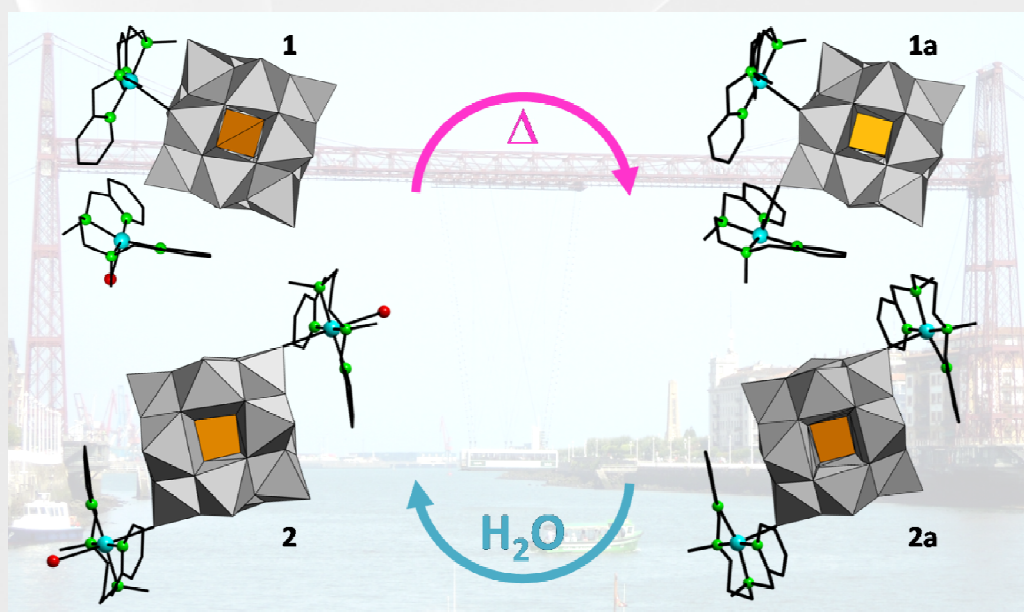
# Single Crystal to Single Crystal transformation promoted by reversible dehydration processes

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KEY WORDS: Polyoxometalates, Hybrid materials, SCSC transformations.

Functionalization of POMs allows for new properties and applications to be obtained because of the synergistic effect between the active inorganic and metalorganic building blocks. Copper complexes represent exceptional moieties for the functionalization of POMs because of the geometrical flexibility of the copper(II) coordination sphere. Tetradentate ligands containing amine and pyridyl groups ( $N_2Py_2$ ) have been successfully applied in the preparation of several transition-metal complexes for catalytic and/or biological studies. Compound  $[Cu(bpmen)(H_2O)][SiW_{12}O_{40}\{Cu(bpmen)\}]$  (bpmen: N,N'-dimethyl-N,N'-bis-(pyridin-2-ylmethyl)-1,2-diaminoethane) was synthesized under hydrothermal conditions. The compound undergoes single-crystal to single-crystal transformation promoted by reversible dehydration process that has been followed by single-crystal X-ray diffraction. The layered structure of the compound shows rows of monodecorated polyanions with complex counter cations occupying intralamellar spaces. Differences in the crystal packing are related to the change in the complex geometry and ligand conformation originating from the introduction of an additional methylene group in the N-(CH<sub>2</sub>)<sub>n</sub>-N bridge. Dehydration of  $[Cu(bpmen)(H_2O)][SiW_{12}O_{40}\{Cu(bpmen)\}]$  promotes coordination of the complex counter cation to the polyanion and consequent formation of a *cis*-didecorated neutral species in the anhydrous compound.



This work has been developed in the research group MOFPOM under supervision of Prof. Juan M. Gutierrez-Zorrilla, Prof. Luis Lezama, Dra. Leire San Felices and Dr. Santiago Reinoso, Department of Inorganic Chemistry, ZTF-FCT.

# The Self-Assembly of Giant Polyoxoanions in solution

*Beñat Artetxe*

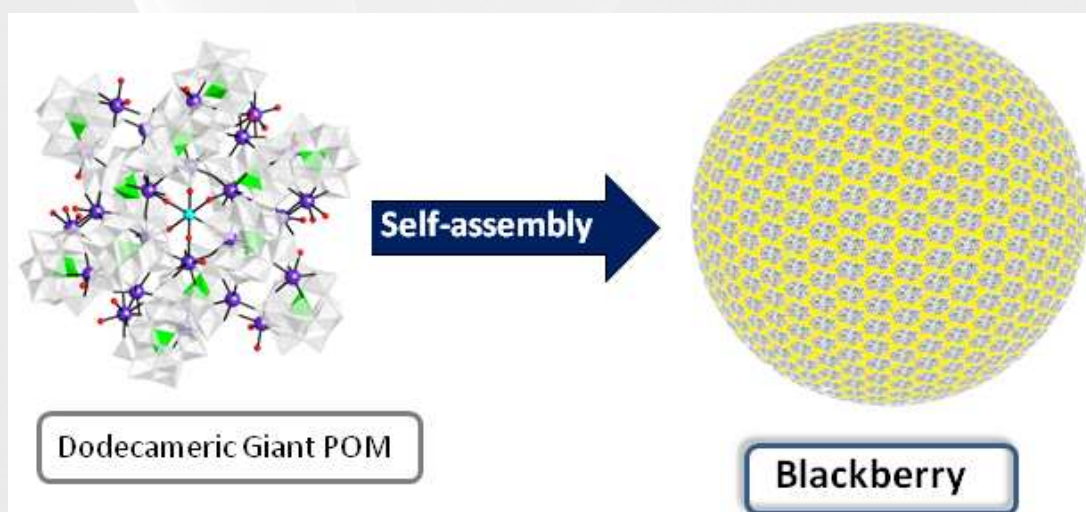
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P. O. Box 644, 48080 Bilbao, Spain

KEYWORDS: Polyoxometalates, Lanthanides, Self-Assembly, Blackberry.

Polyoxometalates (POMs) are a large class of anionic clusters composed of oxo-bridged early transition metals from groups 5 and 6 that show remarkable electronic properties and huge structural diversity. Among the vast POM family, lanthanide (4f)-containing species constitute one of the largest and currently most active groups because combination of POM building-blocks with rare-earth metals has been shown up as a powerful tool for designing new architectures and introducing additional properties (catalytic, optic, magnetic) to the POM system.

Reaction of lanthanide(III) ions with  $\text{GeO}_2$  and  $\text{Na}_2\text{WO}_4$  in NaOAc buffered medium at room temperature results in a library of clusters which consist of cation-directed  $\{\text{Ln}_2\text{GeW}_{10}\text{O}_{38}\}$  (M) dilacunary Keggin fragments stabilized by incorporation of 4f atoms to the vacant sites. For early lanthanides (Ce to Sm), crown-shaped  $\text{M}_6^{35}$  hexameric architectures are obtained in the exclusive presence of  $\text{Na}^+$  cation, whereas the addition of  $\text{K}^+$  cation lead to giant  $\text{M}_{12}^{52}$  dodecameric structures with 120 tungsten and 24 lanthanide atoms per POM cluster. On the contrary, smaller chiral  $\text{M}_2^{12}$  dimeric and  $\text{M}_4^{24}$  tetrameric clusters were formed from mid-to-late lanthanides (Gd to Lu) in the exclusive presence of  $\text{Na}^+$  cation or with the addition of  $\text{Cs}^+$  ion respectively. Among their properties, it is worth highlighting the photoluminescence shown by the Sm, Tb or Dy derivatives.

Giant polyanions, like the obtained  $\text{M}_{12}^{52}$  dodecameric species, are suitable models to understand the gap in the solution behavior between simple ionic solutions (small ions that can be considered as point charges) and unstable colloidal suspensions. POMs cannot be treated as point charges because of their big size, but opposite to colloidal suspensions they form stable “real solutions”. Due to their well defined molecular structure, big size, high negative charge and stability in polar solvents, large POMs with sizes ranging from ca. 2 nm to 6 nm can show unusual behaviors in solution. Clusters slowly self-assemble into spherical, hollow, single-layered and stable vesicle-like supramolecular entities so-called “blackberry” type structures. Laser light scattering (LLS), represents an ideal technique to monitor the self-assembly of diluted POM solutions. Some fascinating biological behaviors such as the self-recognition among molecules take place during the blackberry formation.



This work has been carried out in the MOF-POM lab of this university under the supervision of Prof. Juan M. Gutiérrez-Zorrilla and Dr. Santiago Reinoso.

# New electrodic materials for Li-ion and Na-ion batteries

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KEY WORDS: Li-ion and Na ion batteries, electrochemistry, spinel, sodium vanadium fluorophosphates.

The search for commercially viable Li-ion and Na-ion batteries demands the discovery and optimization of new electrode materials and electrolytes, in order to obtain more economic, safer and longer-life batteries.

A substantial segment of the battery materials community is moving toward developing electrode materials on the basis of abundance and availability of the relevant chemicals. Regarding to lithium ion batteries, lithium manganese oxide spinel is especially interesting for use in hybrid electric vehicles and electric vehicles due to its low cost and high safety. However, the main problem for application is the capacity fading caused by the instability of Mn(III)[1]. In order to improve that factor, we investigate the effect of substitution of a small quantity of Mn by p-block elements such as Ga<sup>3+</sup> or Si<sup>4+</sup>. The Li(Mn,M)<sub>2</sub>O<sub>4</sub> (M = Ga<sup>3+</sup>, Si<sup>4+</sup>) phases have been synthesized by the freeze-drying method and calcinated at 700°C.

On the other hand, the low cost, high abundance and ease of acquisition of sodium minerals promote interest in sodium-based electrochemical systems, especially for stationary energy storage devices. However, significant challenges such as energy density and long term stability must be addressed [2].

In general, Na<sub>3</sub>V<sub>2</sub>O<sub>2x</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3-2x</sub> sodium-vanadium fluorophosphates are good cathodic materials for Na-ion batteries due to their high reaction voltages (at 3.6 and 4.1 V vs. Na/Na<sup>+</sup>) and their good specific capacity values in sodium half-cells (theoretical specific capacity of about 130 mAh/g) which leads to high energy density compounds (ca. 500 Wh/kg) [3].

In this study, two sodium-vanadium fluorophosphate materials were prepared by two different hydrothermal synthesis:

- A mixed valence V<sup>3+</sup>/V<sup>4+</sup> composite material belonging to the Na<sub>3</sub>V<sub>2</sub>O<sub>2x</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3-2x</sub>/C family where 0 < x < 1.
- Na<sub>3</sub>V<sub>2</sub>O<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F phase (x = 1) where vanadium oxidation state is V<sup>4+</sup>.

In the first one, the carbon content in the final product was 6.4% wt., leading to a mixed valence V<sup>3+</sup>/V<sup>4+</sup> compound where x = 0.8 for the Na<sub>3</sub>V<sub>2</sub>O<sub>2x</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3-x</sub> family. The second set of samples was prepared by a different synthesis method with no added carbon in order to get the pure V<sup>4+</sup> Na<sub>3</sub>V<sub>2</sub>O<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F phase (x = 1).

Structural characterization of the composites was performed by powder X-ray diffraction (XRD). Magnetic susceptibility measurements and EPR (Electron Paramagnetic Resonance) polycrystalline spectra were necessary for the determination of the oxidation state of the vanadium. The morphology of the materials was analyzed by Scanning and Transmission Electron Microscopy (SEM/TEM) and the electrochemical measurements were conducted using coin-cell and Swagelok-type cells *versus* a metallic lithium or sodium anode.

[1]. O. K. Park, Y. Cho, S. Lee, H.-C. Yoo, H.-K. Song, J. Cho. *Energy Environ. Sci.* **2011**, 4, 1621 - 1633.

[2] V. Palomares, P. Serras, I. Villaluenga, K.B. Hueso, J. Carretero-González, T. Rojo, *Energy Environ. Sci.*, **2012**, 5, 5884.

# Functionalized magnetic nanoparticles for biomedical applications

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KEY WORDS: nanoparticles, thermal decomposition, superparamagnetism, electron magnetic resonance, magnetic hyperthermia.

In recent years there has been an important advance in the study of magnetic nanoparticles due to their application in different research fields such as biomedicine. The size confinement to nanometer scale in magnetic materials changes the properties from those of the bulk ferro and ferrimagnetic counterparts, the remainder magnetization disappears keeping the magnetic moment. These properties are interesting for some biomedical applications, such as drug delivery, MRI contrast or magnetic hyperthermia. In magnetic hyperthermia, an emerging alternative for the treatment of cancer, the size of nanoparticles, their stabilization and biocompatibility are key attributes that must be controlled. In this sense, nanoparticles must be in biological environment, which requires a proper optimization of the synthesis method and an adequate surface functionalization, which allows a good stability. The most promising materials for such applications are the superparamagnetic iron oxide (SPIO) compounds.

In this work we report the preparation and characterization of  $\text{Fe}_3\text{O}_4$  and  $(\text{Fe}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4)$  nanoparticles to study the changes in magnetic properties.  $\text{Fe}_3\text{O}_4$  nanoparticles have been synthesized by thermal decomposition of iron (0) pentacarbonyl with 1,2-hexadecanediol as dispersant, benzyl ether as solvent and oleic acid and oleylamine as coating. The nickel ferrite nanoparticles have been synthesized using Nickel (II) and Iron (III) acetylacetonates as precursors. The nickel percentage range rises from 3 to 20 percent of nickel.

The chemical, structural, morphological and spectroscopic characterization was performed by thermogravimetric analysis, X-ray diffraction (XRD), Dynamic Light Scattering (DLS) and Transmission Electron Microscopy (TEM). X Ray Diffraction (XRD) technique was used to ascertain that the material preserve the inverse spinel structure without impurities. Dynamic Light Scattering (DLS) and Transmission Electron Microscopy (TEM) studies have concluded that the diameter of magnetic nanoparticles varies depending on the synthetic parameters. The optimization of the synthesis method yields particles from 4 to 15 nm with contents of organic matter in the 15 - 30 % range. It is to note that the seeded-growth method based on successive additions of reagents over previously synthesized magnetic particles leads size tunable nanoparticles with high crystallinity.

In order to study magnetic properties of the samples, magnetization measurements were carried out in function of magnetic field at different temperatures, as well as Electron Magnetic Resonance Spectroscopy (EMR) measurements in dispersed particles assuring a lack of interaction. It has been found a superparamagnetic like behavior for most of the samples with low blocking temperatures. EMR measurements have shown a correlation between the position of  $g_{\text{eff}}$  value and the size of synthesized nanoparticles, and linewidths that vary along with the size dispersion of the nanoparticles. Hyperthermia measurements have been performed for nanoparticles with the highest magnetization values. The magnetic study has also led us to find a relationship between magnetic behavior, size,  $g_{\text{eff}}$  value and hyperthermia response.

# Hydrogen production by catalytic reforming of pyrolysis liquid from lignocellulosic biomass

Aingeru Remiro

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KEY WORDS: Hydrogen, bio-oil, steam reforming, catalyst, CO<sub>2</sub> capture

## HYDROGEN FROM BIOMASS

Hydrogen is an emerging energy carrier and an important chemical raw material for oil refineries, ammonia production, methanol synthesis and other minor applications. The current world consumption of hydrogen has a sustained annual growth forecast of 5-10 % (corresponding to 50 % of the total energy consumption predicted for 2100). Currently hydrogen is mainly obtained from fossil fuels by steam reforming, which results in CO<sub>2</sub> emissions during its production processes. The future hydrogen market, as fuel and energy carrier, is promoted by the need for reducing CO<sub>2</sub> emissions, which requires its production from renewable raw materials and energy sources. Consequently, the forecast until 2100, establishes a transitional scenario from the production of hydrogen from fossil fuels and from water (by electrolysis), in which the emerging raw material is the lignocellulosic biomass, due to its availability and renewable nature.

## OBTAINING AND PROCESSING OF BIO-OIL

Bio-oil was obtained by flash pyrolysis of lignocellulosic biomass in a semi-industrial plant (spouted bed reactor) obtaining a bio-oil yield of 70 wt%. Despite the environmental and technological advantages of obtaining bio-oil, it must be emphasized the difficulty in handling and valorization when bio-oil is heated for subsequent gas phase catalytic conversion due to repolymerization of lignin derived compounds. A solid waste is formed denoted as pyrolytic lignin (according to its origin) leading to operation problems and catalyst deactivation. Our research group has used a two steps in line process in order to solve this problem: a thermal step (without catalyst) where pyrolytic lignin is retained and ii) a catalytic step where the reforming reaction takes place. The use *in situ* of a CO<sub>2</sub> adsorbent (dolomite) in the reactor enables the WGS reaction to shift its thermodynamic equilibrium, increasing H<sub>2</sub> yield and selectivity. The energy balance of the process is an additional advantage because the carbonation is an exothermic reaction.

## RESULTS AND DISCUSSION

Ni catalysts supported on alumina achieve the best compromise between bio-oil conversion, H<sub>2</sub> yield and low deactivation in the reforming of the aqueous fraction of bio-oil. Bio-oil conversion is complete for 5 h at 700 °C, with H<sub>2</sub> yield of 94 % (stoichiometric), low CO yield (10 %) and nule of CH<sub>4</sub>. At these operating conditions CO<sub>2</sub> in situ capture increases H<sub>2</sub> yield up to 99 % and the H<sub>2</sub> selectivity is almost 100 %, which facilitates the subsequent purification steps of products stream.

Raw bio-oil has been reformed succesfully with the technology used (two step process) maximizing its valorization. 700 °C is the optimum reforming temperature since a compromise is achieved between deactivation by coke deposition (at low temperature) and Ni sinterization at higher temperature.

The proposed technology is effective for obtaining H<sub>2</sub> at large scale from the bio-oil produced offshore from lignocellulosic biomass using simple and environmentally friendly processes. The advantages of the proposed technology (high conversion and purity of H<sub>2</sub>) are highlighted when compared to the results in the literature, while the lower productivity values are compensated obtaining a recoverable product (pyrolytic lignin) in the thermal step. It is also worth mentioning the attenuation of catalyst deactivation compared to other systems.



# Tertiary recycling of polyolefin plastics

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KEY WORDS: pyrolysis, polyolefins, light olefins, hydrogen, conical spouted bed

## PYROLYSIS OF POLYOLEFINS

Plastic waste pyrolysis (thermal cracking under inert atmosphere) is considered one of the most feasible recycling methods to obtain gas or liquid fuels or to recover monomers, which contributes to preserving the environment and intensifying petroleum valorisation. Plastic, and specially polyolefins (2/3 of waste plastics), pyrolysis can be carried out in small units and close to collecting points, avoiding the costs currently attached to plastic waste transports. Thermal pyrolysis at low temperature and low residence time gives way to a product stream made up of waxes that can be stored and transported to refinery, being suitable feed for FCC, hydrotreatment or steam cracking units. An alternative to transport waxes to refinery is to advance in their valorisation by downstream thermal or catalytic cracking to obtain light olefins or fuels, whose ultimate end use will be their inclusion in the corresponding refinery pools, for their treatment and commercialization by means of the usual procedures. Therefore, plastic pyrolysis viability is directly related with the integration of the process into actual refineries.

## POLYOLEFINS PYROLYSIS PRODUCTS

The continuous catalytic pyrolysis of high density polyethylene (HDPE) has been carried out in a two-step reaction system involving a pyrolysis conical spouted bed reactor followed by a downstream cracking. Given the low thermal conductivity and sticky nature of the plastic materials, a reactor with high heat and mass transfer rates is essential in order to minimize the limitations involving the physical steps prior to devolatilization and to ensure isothermal conditions. The conical spouted bed reactor (CSBR) used in this study is especially suitable for the continuous pyrolysis of HDPE, even at low temperatures due to the minimization of the physical limitations by the vigorous cyclic movement of the particles in this reactor. Given the low residence time of the gases in the CSBR and the low pyrolysis temperature used (500 °C), the product stream obtained in the pyrolysis step is composed mainly of C<sub>12</sub>-C<sub>20</sub> hydrocarbons and waxes, with the overall yield being 90 wt%. Furthermore, the other products obtained (non-aromatic C<sub>5</sub>-C<sub>11</sub> hydrocarbons, light olefins and alkanes) can be upgraded by cracking. Moreover, it should be noted that apart from the good quality of the product stream obtained for the downstream cracking, continuous operation allows obtaining a constant stream at the outlet of the first step, which is essential to ensure an accurate study of the influence of second-step operating conditions.

## SELECTIVE PRODUCTION OF LIGHT OLEFINS OR HYDROGEN

The high yield and selectivity of waxes in a CSBR has allowed their downstream transformation to obtain high value added products such as light olefins or hydrogen. Three different alternatives have been studied: i) thermal cracking at high temperature obtaining high yields of light olefins (77 wt% at 900 °C), with individual yields of ethylene, propylene and butenes, of 40.4, 19.5 and 17.5 wt %, respectively; ii) catalytic cracking (catalyst based on HZSM-5 zeolite) to obtain high yields of light olefins (62 wt% at 500 °C) with the individual yields of ethylene, propylene and butenes being 10.6, 35.6 and 16.7 wt%, respectively; iii) reforming (Ni/Al<sub>2</sub>O<sub>3</sub> commercial reforming catalyst) to obtain a product stream mainly composed of hydrogen (70 vol%). Therefore, alternatives of thermal cracking, catalytic cracking and reforming are suitable for the selective production of ethylene, propylene and hydrogen, respectively. Moreover, it should be noted the high efficiency of three strategies studied, obtaining total conversion of waxes (main product in the first step) at zero time on stream in all cases.

# Quantum Simulators

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KEY WORDS: quantum physics, quantum information, quantum optics.

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One of the most relevant contributions of the 20th century to knowledge has been the computer, a machine capable of running an algorithm further than what any human being can do it. Computers have become an essential tool in research, allowing scientist to see what happens there where the analytical methods become too hard or even impossible. However, computers, which codify information in a classical manner, hit their limit when they try to reproduce models of quantum physics. It was Richard Feynman in the early 80's who proposed the concept of quantum simulators as a path to overcome this limitation. Quantum simulators are systems that naturally behave in a quantum manner and which we manipulate to make them imitate quantum models of interest. These systems are designed in ways that allow the access to magnitudes of interest, magnitudes that in the system where they appear naturally are inaccessible. These systems are called quantum platforms and run from trapped ions to superconducting circuits, including cold atoms and many others, which are then manipulated through laser fields, magnetic fields, electric potentials... The work that we develop in Bilbao consists in the theoretical proposal of these designs, as an example we can mention the proposal for the implementation of the Dirac equation in superconducting circuits. In the same way we also work in the conceptual enhancement of quantum simulators, or quantum information in general. In this sense, we have the proposal of Embedding Quantum Simulators made in Bilbao, a new paradigm in quantum simulators allowing the efficient access to magnitudes that are not defined as the expectation value of observables in the frame of quantum mechanics, as is the case of some measures of entanglement.

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Idatzizko komunikazioak (Posterrak)

# **ABSTRACTS**

Comunicaciones escritas (Pósters)

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# Biozientziak: Ingurune alderdiak



# Biociencias: Aspectos ambientales

# Understanding disorders of the visual system and promoting repair and regeneration

## Neuro-ophthalmo Biology Group

*Elena Vecino*<sup>1</sup>, *Jennifer R. Higginson*<sup>1</sup>, *Noelia Ruzafa*<sup>1</sup>, *David Rodríguez Fernández*<sup>1</sup>, *Juan Durán de la Colina*<sup>2</sup>, *Javier Araiz*<sup>2</sup>, *Javier Haritz Urkola*<sup>3</sup>, *Alex Fonollosa*<sup>4</sup>, *Marta Galdós*<sup>4</sup>, *Sergio Pinar*<sup>4</sup>

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KEY WORDS: retina, cornea, glaucoma, uveitis, neuroprotection, retinal ganglion cells, glia, computational, ocular surface, primary cell cultures.

We are a multidisciplinary group consisting of ophthalmologists, biologists, biochemists, physicists and veterinarians and currently have 15 members. We have been working together for the last 18 years. Our group has been recognised by the Basque Government and they awarded us with 6 years of funding from 2010-2015. Our lab is located in the Faculty of Medicine in the Department of Cell Biology and Histology but members of the group also work in Hospitals such as Cruces, San Eloy, Donostia and Txagorritxu. The director of the group GOBE (Grupo de Oftalmo-Biología Experimental) [www.ehu.es/GOBE](http://www.ehu.es/GOBE) is Prof. Elena Vecino from the Faculty of Science and Technology.

Within GOBE there are four main areas of research:

1. **Neuroprotection** of retinal ganglion cells by retinal glia (PI: Prof. Elena Vecino). Understanding the molecular mechanisms that lead to the death of retinal ganglion cells (RGCs) in retinopathies such as **glaucoma**. RGCs are neurons that transport visual signals from the retina to the brain and their loss, after disease or injury, leads to irreversible blindness. By studying the molecular interactions between RGCs and glia, which are the supportive cells of the retina, we hope to understand how we can prevent cell death and instead promote RGC regeneration. In this project we collaborate with researchers at the University of Salamanca, Cambridge University and New York Medical College. The **computational** non-invasive characterisation of cellular changes within the normal and pathological retina is an aspect that the group is interested in and we are currently collaborating with physicists from UPV/EHU and Bordeaux University.
2. **Ocular surface** regeneration (PI: Prof. Juan Durán). Focussed on researching factors present in the tears, that can promote the repair of the injured ocular surface, in particular the corneal epithelium. In this project we have been collaborating with a proteomics expert, Prof. JM Arizmendi at the FCYT.
3. **Analysis of aqueous humor in glaucoma** patients (PI: Dr Javier Haritz Urkola). Analysing the viscosity of aqueous humor in patients with glaucoma to detect any changes compared with healthy patients. Aqueous humor is a transparent, gelatinous fluid that is secreted from the ciliary epithelium and is located in the space between the lens and the cornea. Alterations in its composition may help us understand more about how glaucoma progresses.
4. **Uveitis** (PI: Dr. Alex Fonollosa) Uveitis is a general term describing a group of inflammatory diseases that produces swelling and destroys eye tissues. Dr Alex Fonollosa's group are interested in understanding more about uveitis and are currently studying retinal cell cultures to test the possible action of somatostatin in the tight junctions formed in the retina-pigment epithelium. These basic studies are done in collaboration with SGIker and biotech companies with the aim of developing clinical applications.

Together we have a shared interest in studying disorders of the visual system using different approaches. A total of 10 PhD theses have been supervised by members of GOBE in the last 10 years and 7 more are being carried out at present, as well as several Masters and Graduate theses.

**Investigative Techniques** used in our research are: immunohistochemistry, electron microscopy analysis, primary cell cultures of retinal cells, organ-explant cultures, eye microsurgery, animal models (ischemia and glaucoma), computer vision.

# Study and integration of ecosystem services in a sustainable land management

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KEY WORDS: Ecosystem services, Indicators, Mapping, Models, Participatory process, Perception, Scenarios.

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The aim of our research group is to analyze the structure and functioning of the socio-ecosystems in order to provide the information and tools required by the decision-makers for a sustainable land management. A sustainable management must value, maintain and improve ecosystems and their global change adaptability to promote society well-being.

In this context, we are performing the following actions:

1. Identification and analysis of state and evolution of ecosystem services in the last decades by means of 60 indicators.
2. Mapping ecosystem services at different spatial scales (CAPV, Bizkaia, Lea watershed, Urdaibai, Bilbao Metropolitan Greenbelt...), using GIS programs. Some of these services are: Carbon storage, Water Flow Regulation, Natural diversity conservation, Recreational use, Aesthetic quality of landscape...
3. Use of models to develop future scenarios to analyze the consequences of the decisions on the flow of ecosystem services.
4. Analysis of perception and demands by society of ecosystems services, by means of participatory processes.
5. Analysis of the applicability of the information generated in the project: mechanisms and pathways to integrate this information into the decision-making processes.
6. Development of new tools to facilitate decision making: multi-functionality indicators.
7. Disclosure of the concepts and results.

## Acknowledgments

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# Ecophysiology of Plant Stress and Soil Contamination (EKOFISKO)

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PROFESORES: José M<sup>a</sup> Becerril (I.P.), José I. García, Antonio Hernández, Raquel Esteban.

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KEY WORDS: Environmental Stress, Biomarkers, Extreme environments, Nutraceutic, Photoprotection, Phytoremediation,

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Since 1990 The EKOFISKO group has developed research and teaching activities on physiological and ecophysiological aspects of natural and anthropic agents causing stress in plants. Our group is a consolidated research group of the Basque Government composed of 8 PhD, 2 PhD students and 3 degree students.

This group has developed a variety of novel methodological tools: (i) determination of plant stress biomarkers, in particular those related to photoprotection and oxidative stress, (ii) set up of plant toxicity bioassays to determine the ecotoxicological effects of pollutants in contaminated soils, and (iii) implementation of physiological parameters to evaluate phytotoxicity or damage caused by natural stress conditions as extreme temperatures, drought, light intensity, nutritional disorders, etc. Recently, in collaboration with other groups, we have incorporated genomic methodologies with emphasis in differential gene expression and in the application of DNA microarrays to assess and monitor soil health in a multidisciplinary approach.

All these methodologies have been implemented in several more applied research areas:

- Determination of the role of photoprotective compounds and tolerance to stress conditions (natural or anthropic) with particular emphasis on the acclimation to extreme environmental conditions, such as those prevailing at high altitudes, forest understory or historically polluted sites.
- Use of plant biomarkers to monitor environmental and global change and genotype plant selection for tolerance to adverse climatic agents and phytoremediation.
- Identification of environmental agents to enhance nutraceutical compounds (carotenoids and tocopherols) in plant foods.
- Use of plants for ecological restoration of degraded environments, specially polluted soils through ecotechnologies as bio- and phytoremediation (phytostabilization, phytoextraction and rhizodegradation).
- Assessment and monitoring soil health with biological indicators during remediation processes.

The research indicated above is currently carried out in a multidisciplinary approach in collaboration with relevant national and international scientists, universities (Complutense de Madrid, Autónoma de Barcelona, La Laguna, Helsinki, La Frontera, Tartu, Australian National, Innsbruck, etc) and institutions (Neiker, Gaiker, Phytosphere Institute, Royal Kew Gardens, USDA, etc), and supported regularly by many competitive projects.

The quality of group's achievements is supported by regular publications in international journals (43 in the last 5 years), and by regular participation in national and international congresses. We also have a compromise on the cooperation for development, with several projects in Latin American universities (Chile, Nicaragua and Cuba). Besides, not only our group is very active in the formation of PhD students, but also we participate in three Official Master Programs: "Agrobiología Ambiental", Environmental Contamination and Toxicology and "Enología Innovadora" and in the Doctorate Program "Agrobiología Ambiental". The latter has been honored with a quality award by the Ministry of Education.

# Diversity, Ecology and Conservation of Macrofungi

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KEY WORDS: Ascomycota, Basidiomycota, community-ecology, Mycorrhizas, wood-inhabiting fungi Soil contamination, Revegetation, Global Change

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Fungi are one of the oldest and most diverse group among living organisms. Currently, molecular analyses are revealing new insights in the understanding of fungal phylogenetic relationships and therefore their phylogenetic classification and taxonomy is continuously updating. According to their ecological roles, fungi are considered a key group in the ecosystems functioning, as they play vital roles in processes such as decomposition, nutrient cycling and nutrient transport. Due to the phylogenetic diversity and ecological roles of fungi, they offer a great variety of possibilities for research. In this way, The Mycology Group has developed several research lines.

The first research line aims to expand the knowledge of the taxonomical diversity of macromycetes (especially Basidiomycota). In this way, in collaboration with researchers of the Botanical Gardens from Madrid and Lisbon, we are currently studying the taxonomical diversity and biogeographical interconnections of the corticioid fungi of the Iberian Peninsula and the Macaronesian Region. This project is divided into three main parts: Part I) Azores, Madeira and Canary Islands; Part II) Cape Verde and the northwest coast of Africa; Part III) Exploring the hidden diversity of Macaronesian fungi. In this research line can also be mentioned the PhD project titled “*The order Cantharellales in the Iberian Peninsula and the Balearic Islands*” defended by Ibai Olariaga in 2009.

The second research line is focused on fungal ecology and conservation, for what we investigate how the environmental factors affect the fungal community. In this way, the PhD student Nerea Abrego is studying how the habitat degradation and fragmentation of beech forests are influencing the wood-inhabiting fungal community. With the objective of giving sustainable forest management recommendations to forestry managers, this PhD project covers the following topics: I) The effects of habitat degradation on the composition and structure of wood-inhabiting communities; II) The effects of forest fragmentation on wood-inhabiting communities; III) Spatial scale effects on wood-inhabiting fungal community turnover; IV) The effects of habitat degradation and fragmentation on species-to-species associations and interactions.

Another research line is related to mycorrhizal fungi, which are the group of species that compose complex relationships with plant roots. Our research is focused on the mycorrhizal interactions of *Alnus* tree-species (alder). The alder is one of the few species that is able to establish three types of mutualistic associations in their roots, from which two are mycorrhizal. Much of the ecology of this tree species can be understood under these interactions, as mycorrhizal interactions enable this tree species to be pioneers in habitat colonization, fast-growing, and able to grow in extreme conditions.

Finally, and related with fungal conservation, we want to mention the project “*Evaluation of the threat level of the threatened species from the preliminary Red List of Fungi of the Basque Country*”, which has been financially supported by Ihobe. This project represents the first attempt to evaluate the threat of fungal species that were previously red-listed in the Basque Country (project led by Isabel Salcedo).

Our work can be framed up in answering ecological questions that derive in recommendations for the design of effective protection area networks for the conservation of the fungal diversity.



# Group for the study of Microalgae at the University of the Basque Country

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KEY WORDS: Microalgae, Toxic Phytoplankton

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Phytoplankton are the autotrophic component of the plankton community and the main responsible of primary productivity in the ocean. Furthermore, phytoplankton can be a source of problems, when toxic species are present or the density of the community is very high. This is the reason for monitoring the phytoplankton community along the Basque coast or in the Bilbao estuary. Due to the difficulty of identifying the organisms of the community with the monitoring routine techniques to a species level, in our laboratory some phytoplankton groups have been analyzed using some other different techniques. About Haptophytes and Cryptophytes, more than 20 species of each group have been isolated, describing the new species *Prymnesium palpebrale*, *Urgorri complanatus*, *Teleaulax minuta* and *T. gracilis*. Among diatoms, we have focused on the toxic genus *Pseudonitzschia*, identifying more than ten species, with *P. plurisecta* and *P. abrensis* as new species. Apart from the water column, microalgae can be found in the benthic zone, where toxic dinoflagellates have been studied during the last years with special attention due to the problems they can cause in tropical waters. At the Basque coast, we have detected the presence of genus *Ostreopsis*, which causes some toxicological problems at the Mediterranean Sea.

# Plants towards climate change: possible CO<sub>2</sub> sinks and bioenergetic crops

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KEY WORDS: Bioenergetic crops, climate change, CO<sub>2</sub> sinks, plant physiology and production

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The rise of atmospheric CO<sub>2</sub> may alter the global climate raising temperature and modifying the rainfall pattern exacerbating even more the risk of drought and salinity, especially in the Mediterranean region, reducing drastically the productivity of the crops. Furthermore, these alterations can also modify the interactions between plants, provoking variations in biodiversity.

So, climate change raises important scientific challenges for plant physiologists. Firstly, we need to expand and broaden our knowledge about the responses of plants to the environment, so that we can predict the impact of climate change on the growth of the crops and natural ecosystems. Secondly, the understanding of the response of the plants to climate change provides us tools and knowledge to minimize the potential negative impact. Plants through photosynthetic activity function as excellent sinks of environmental CO<sub>2</sub> reducing the effects of climate change and contributing to the Kyoto compliance. On the other hand, the produced biomass could have an energetic use. However, those perspectives can be altered by factors such as limitation of nutrients and water, temperature rise, salt stress and/or other factors related to the rise of CO<sub>2</sub> that can affect physiology and productivity of the plants.

Thus, the objective of this research group is focused on the analysis of different factors associated with climate change that affect physiology, growth and productivity of the plants in the nowadays changing environment such as atmospheric CO<sub>2</sub>, water availability, soil salinization, NO<sub>3</sub><sup>-</sup> availability, temperature, as well as interactions within them and plant-plant interactions. We also investigate if the plants will be able to adapt to these new environmental conditions, if as the result of these climatic changes would be necessary to find new varieties of the species currently used in agriculture or whether it would even be necessary to find other species better adapted to new climatic conditions.

At the same time, we intend to take advantage of the capacity of the plants themselves to kidnap the excess of environmental CO<sub>2</sub> permitting that way a longer period of C retaining, eventually using plants as biomass source for utilization as renewable bio-fuels.

# Integrating levels of biological complexity for the assessment of the long-term trends in ecosystem health in the estuary of Bilbao (Bay of Biscay): 2000-2009

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Ecosystem health; Estuary of Bilbao; Bay of Biscay;

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The small macro-mesotidal estuary of Bilbao is located in the Bay of Biscay (43°23' -43°14' N, 3°07' -2°55' W). It is an intensely modified (reclamation, dredging and channelization) narrow (33-270 m wide) ~14.5 km long artificial channel that crosses urban and industrial areas and ends in a 3.8 km wide and 10-30 m deep semi-enclosed embayment known as Abra, which has undergone large harbour developments. From the mid 19th century, water and sediment quality and ecosystem health were significantly impoverished as a consequence of huge amounts of untreated domestic sewage and heavy industrial wastes. For many years, hypoxic/anoxic conditions developed throughout the estuary and high significant losses in biomass and diversity were registered in biological communities (including the existence of dead zones in inner estuary). However, since the late 1980s, the metropolitan area of Bilbao underwent a substantial transformation of its economy with replacement of most polluting industries in parallel with the progressive implementation of an integrated sewage treatment plan. A recovery trend in estuarine health status has been reported at different levels of biological complexity during the last two decades. Integrating these biological complexity levels may provide new insights into the assessment of the long-term trends in ecosystem health. Within this framework, bioaccumulation, biomarkers and disease in sentinel species, phytoplankton and zooplankton communities and physical-chemical variables recorded since 2000 were integrated for assessing the long-term trends in the health status of the estuary. This approach revealed a general recovery trend from 2000 to 2009, with sporadic critical events of diverse degree of incidence such as, for instance, regular dredging activities and the Prestige oil spill that affected the region between 2002 and 2005, at least.

# Enzyme and Cell Technology

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KEY WORDS: enzyme, biocatalysis, microalgae, cyanobacteria, magnetic nanoparticles (MNPs), cross-linked enzyme aggregates (CLEAs), chiral hydroxyalkanoic acids, biodiesel, biosurfactants, CO<sub>2</sub> sink, added-value

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The main goal of the Enzyme and Cell Technology Group is the **use and development of nanotechnologies** which employ **biocatalysts** (isolated enzymes or microbial cells) for **industrial, environmental or biomedical applications**. The Group has experience and equipments for the production, purification and characterization of proteins and enzymes with industrial or biomedical interest. For this purpose there are available techniques to culture heterotrophic (bacteria, yeasts and fungi) and phototrophic (eukaryotic microalgae and cyanobacteria) microbial cells in orbital incubators or bioreactors (fermentors and photobioreactors). Also there are available technologies for the immobilization of biocatalysts by adsorption or covalent-linking onto solid supports and entrapment in polymeric matrices which allows their use in reactors of different design and operation modes at laboratory scale.

Recently, other nanotechnologies have been developed for the synthesis and functionalization of magnetic nanoparticles with enzymes or cross-linked enzyme aggregates (CLEAs) of interest in industrial biotechnology and biomedicine. Thus, lipases have been immobilized to catalyze the transesterification reactions to produce biodiesel and biosurfactants as well as polyhydroxyalkanoate depolymerases, enzymes capable to degrade bioplastics in order to obtain chiral monomers for the synthesis of bioactive compounds of interest in pharmacy or other functionalized bioplastics. Also intensive cultures of microalgae in helicoidal photobioreactors showing remarkably tolerance to CO<sub>2</sub> are being investigated as components of new biological CO<sub>2</sub> sinks of utility to mitigate the release to the atmosphere of industrial gas effluents. The resulting cell biomass will be evaluated as a source of biotechnological added-value products and of reserve oils or polysaccharides of interest to produce biodiesel or bioethanol, respectively.

Among the available analytical or preparative techniques are remarkable the use of VIS/UV spectrophotometry, preparative (LPLC y FPLC) and analytical (HPLC) chromatographies, and electrophoresis (isoelectrofocussing, native PAGE, SDS-PAGE, 2D-PAGE) for the separation and characterization of proteins and nucleic acids. Moreover, the Group possesses facilities and experience to carry out techniques for protein isolation and characterization, enzyme assays, protein cross-linking, image analysis, and the design and operation of lab-bench bioreactors and photobioreactors. Also molecular biology techniques for gene cloning, PCR, and for the expression, purification and characterization of recombinant proteins are available.

At present, the on-going **basic and applied** projects are:

- Enzymic degradation of bioplastics for producing **chiral monomers**
- Enzyme expression in thermophilic cyanobacteria
- Synthesis and functionalization of magnetic nanoparticles with enzymes and cross-linked enzyme aggregates (CLEAs) to obtain biodiesel and biosurfactants
- Utilization of microalgae as a CO<sub>2</sub> sink and as a source to obtain biofuels and other added-value products
- Catalysis of ester-forming reactions in non-aqueous media to synthesize biodegradable polymers

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# Biomembranes and new therapeutic approaches

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KEY WORDS: Bacterial conjugation/Antibiotic resistance/Environmental plasmidome/ Bacterial biofilms/Solid Lipid Nanoparticles

## Coupling proteins of bacterial conjugative systems as drug targets

Due to the existing antibiotic pressure, bacteria have acquired new antibiotic resistances, causing infections and diseases. Bacterial conjugation is the main process responsible for the dissemination of antibiotic resistance genes among bacteria. Therefore, it is necessary to develop new antimicrobial strategies where new antibiotics are combined with inhibitors of proteins essential for bacterial conjugation. Coupling proteins (T4CPs) essential for conjugation. Since this family shares a high sequence homology, results obtained in one member of the family could be extrapolated to different bacteria. The study of their molecular mechanism could be the first step to develop specific inhibitors that could stop the transfer of genetic information among bacteria. The objective of this project is to identify new compounds of therapeutic interest to prevent the dispersion of antibiotic resistance genes in bacteria by inhibiting the activity of T4CPs.

## Membrane proteome of biofilms searching for therapeutic targets against chronic infections

Bacterial biofilms cause chronic infections, including those associated to medical devices that are 10 to 1000-fold more resistant to antibiotics than planktonic bacteria. Biofilm formation is generally considered the most important factor in the pathogenesis of *Sataphylococcus epidermidis*.

Comparative membrane proteomic analysis of the non-pathogenic strain *S. epidermidis* CECT 231 was carried out using three different methods and proteins involved in virulence have been found as more abundant in biofilm state. In particular, Accumulation associated protein (Aap) could be a good therapeutic target to control biofilm infections.

## Environmental plasmidome

Intensive treatment of antibiotics to livestock makes agricultural soils amended with manure and slurry represent an important source of multiresistant bacteria that can infect people through different ways and cause disease outbreaks difficult to control with antibiotics. In this sense, the study of the transferome (conjugative plasmids) of agricultural soils can provide study of great interest. Moreover, bacteria present in soils undergoing chronic heavy metal contamination have shared through conjugative plasmids metabolic tolerance strategies necessary to survive in that environment. Therefore, the soil transferome these conjugative elements, could also be worthy of study.

It is interesting to draw a map of conjugative plasmids present in agricultural soils fertilized with manure animal and mineral soils subjected to chronic contamination with heavy metals. That information will lead us to the analysis of the potential risk of agricultural soils as source of resistant bacteria to large number of antibiotics, by studying the number of resistances of the bacteria present in these soils.

## Solid Lipid Nanoparticles

Colloidal systems have been developed for drug delivery, among them solid lipid nanoparticles (SLN) have been very promising, in particular for oral and topic delivery. SLN are biocompatible and biodegradable entities, and consist of a lipid matrix that should be solid at room and body temperatures. The average particle size should be between 50 and 100 nm. Solid lipids are preferred to liquid oils because drug mobility in a solid lipid is much lower than in a fluid lipid, thus leading to a more gradual release.

An important advantage of SLN as drug delivery systems is that they are made of substances generally recognized as safe for oral and topical administration.

# Genomic Resources: Metagenomics

<http://www.genomic-resources.eu/>

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KEY WORDS: Planktonic Diversity; Massive Sequencing; Amplicon genomics; Metatranscriptomics.

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"Genomic resources" is a Consolidated Research Group for the Department of Education, Universities and Research of the Basque Government (2010-2015). We study living organisms under a genomics perspective. We are keen in DNA variation: statistical analyses of genetic markers, and bioinformatics analyses of DNA sequence data are the expertise of the group. Our contribution spans to different subsets of bioscience, from Animal Conservation and Genetic Improvement Programs, to Forensic Genetics and Personalized Medicine, through Sustainable Fisheries and Aquaculture. Very recently, we launched a new research line focused on environmental diversity of microbes by Metagenomics. This approach – genomics on a huge scale – enables a survey of the different microorganisms present in a specific environment, such as water or soil, to be carried out.

## **Deciphering microbial communities associated to grapevines: the study of Txakoli's varieties**

In the 19th century, agrochemical products allowed the development of the intensive agriculture, but currently it is well known the environmental problems that may cause, i.e. contamination by heavy metals. That is why alternatives to these chemicals are being searched. One of the most promising alternatives is based on the use of biological products, such as plant-associated bacteria that promote plant health and growth.

Our investigation is focused on the bacteria associated to grapevine: the most cultivated fruit crop in the world, with a significant economic and social relevance in the Basque Country.

The overall objective of the project is to define the core of grapevine-associated bacteria (taxa that are shared among  $\geq 95\%$  of the individuals) and to discern the main factors determining it. To achieve this aim we have raised three specific objectives: (1) To establish the bacterial community associated to three varieties of vines traditionally used to produce "Txakoli" wine, and to compare it with the varieties "Riesling" and "Merlot". (2) To determine the impact of heavy metals on vineyard's bacterial diversity, and (3) to establish the soil bacteria succession when transforming a meadow into a vineyard.

The methodological approaches we are developing include the use of NGS (Next Generation Sequencing) technology (Illumina Mi-Seq) and bioinformatic tools (QIIME). Bacterial taxonomic diversity will be analysed by amplicon metagenomics of SSU16S gene.

## **Unravelling the taxonomic and functional diversity of estuarine plankton in the Bay of Biscay**

Planktonic communities are a diverse group of organisms that live in the water column and are incapable of swimming against the current. They provide a crucial source of food to many large aquatic organisms. In addition, and due to their quick responses to climate change and pollution, they provide an early-warning alert to face both anthropic impacts, allowing the design of appropriate adaptation measures.

The first goal in this study is to build a reference map of the planktonic diversity in the Bay of Biscay: (1) Taxonomic diversity will be characterized by identifying and comparing the planktonic taxa (bacterioplankton, phytoplankton and zooplankton) present in two estuaries with different levels of anthropogenic pressure: Nervion and Urdaibai. Within each estuary, a salinity gradient will be analysed monthly along the whole year. NGS technologies will be applied to perform amplicon metagenomics of SSU16S/18S genes. (2) Functional diversity will also be assessed by identifying and comparing the group of planktonic genes active in both estuaries. A metatranscriptome sequencing by NGS will be done.

Our final goal is to develop an accurate, straightforward and cost-effective method for plankton monitoring. Applicable as a tool for early detection of climate change, pollution, invasive species, ... that could lead to adaptation/mitigation measures.

# Molecular Biology of Cancer

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KEY WORDS: Cancer, Cell Cycle, Cell Signaling, Ubiquitination, Gene knockout, Genomics, Proteomics.

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The main feature that defines tumor processes is the alteration of cellular homeostasis. Deregulation of the cell cycle, abnormal intracellular signaling, and defects in protein posttranslational modifications are among the mechanisms that contribute to this alteration. The detailed characterization of these mechanisms, and how they contribute to the neoplastic transformation constitute the main objectives of our research group. Their elucidation could contribute to the search for new therapeutic strategies for cancer treatment.

Our research group is a multidisciplinary team whose components are specialized in the areas of genetics, molecular and cellular biology, proteomics, and bioinformatics. The group has been working for more than a decade in the field of molecular biology of cancer, considered to be a strategic research field by the Euskampus initiative of the UPV/EHU, because of its biomedical and social relevance. The research team has been recognized and funded by the Department of Education of the Basque Government as "Consolidated Group" continuously since 2001.

Research in Biomedicine has experienced an extraordinary revolution in recent years, with the development of technologies that allow the analysis of complete sets of genes and proteins in a particular cell or organism. This has led to the birth of the novel fields of Genomics and Proteomics. We are applying genomic and proteomic approaches, together with classical methods of genetic and biochemical analysis, to identify and characterize the proteins and pathways that play a key role in the control of cellular proliferation and cell fate, including the dysregulation that contributes to oncogenesis. Current areas of research in the laboratory focus on the following topics:

- 1) **RESEARCH LINE 1: Cell cycle regulation by the E2F transcription factors**
- 2) **RESEARCH LINE 2: Small GTPases and their impact on intracellular signaling**
- 3) **RESEARCH LINE 3: Ubiquitylation and nucleocytoplasmic transport of proteins in tumor development**
- 4) **RESEARCH LINE 4: Development and application of proteomic technology**

# Human Molecular Evolution

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KEY WORDS: Neanderthal, Next Generation Sequencing, Paleogenome, bioinformatics, skin pigmentation, melanoma, genetic expression, human diversity, resequencing, aptamer

## **PALEOGENOMICS: RECONSTRUCTION OF THE HUMAN EVOLUTIONARY HISTORY**

The aim of our research is to understand the evolutionary success of our species using paleogenomics analysis. The development of the Next Generation Sequencing (NGS) techniques allows the comparison of the genomic data of our species with other closely related extinct species as Neanderthals. Other aim of our study is to understand the evolutionary process of our species, as well as, the influence on the genomic evolution of environmental and cultural factors. For this purpose, we try to identify the specific genomic variants of our lineage, by establishing genomic differences with contemporary human species. On the other hand, this techniques allow to analyze the genomic variation that existed in the past both intraspecific and interspecific level.

## **PIGMENTATION OF SKIN AND MELANOMA**

There are genetic and environmental factors that determine the risk to melanoma susceptibility. In particular, light-skinned individuals are less protected against photocarcinogenesis and/or photoaging after solar irradiation, especially in recent years, when UV radiation has increased due to the weakening of the ozone layer. Therefore, we are trying to identify genetic variation associated with skin pigmentation in humans, in order to infer its adaptive value and assess its biomedical implications. For that reason, we are focusing on the detection of differentially expressed genes in melanocytic cell lines from individuals with different skin pigmentation, using expression chips (Affymetrix). Subsequently, a subset of loci is selected to analyze their sequence diversity by resequencing and their variation in the copy number of their exons. The variability discovered is analyzed in collaboration with other laboratories, in melanoma patients and healthy individuals. We are evaluating the adaptive value of these polymorphisms by means of bioinformatics and trying to infer the potential biomedical implications (predisposition to cutaneous melanoma). On the other hand, we design aptamers, single-stranded oligonucleotides that bind with high affinity to the  $\alpha$ -MSH hormone, a ligand of *MC1R*. These aptamers will allow the detection and the quantification of the hormone in individuals of light and dark skin pigmentation, and they may also serve as tumor markers for clinical diagnosis of melanoma.

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# 17q21.31: A genetic puzzle.

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KEY WORDS: MAPT, haplotype H2, population genetics.

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17q21.31 is a very unusual genomic region with a highly complex architecture located in human chromosome 17. There is no recombination over approximately 1.8Mb and there appear to be two haplotypes clades, H1 and H2, encompassing an inversion polymorphism containing several genes.

Most work in this region has been focussed on disease susceptibility since H1 is a risk factor locus for several neurodegenerative diseases known as tauopathies while the large number of segmental duplications and their orientation in H2 allele may cause the 17q21.31 microdeletion syndrome. Only a few studies have looked at the population genetics of 17q21.31, which turns out to be extremely interesting. The H1 haplotype occurs in all populations and the H2 clade, in contrast, shows an almost complete association with populations of European ancestry. It has been suggested that the H2 haplotype is under selection in the Icelandic population and that it could be a Neanderthal heritage.

In order to explain the origin and the evolutionary history of the haplotypes, the remarkable geographic distribution of the allele frequencies, as well as the role of natural selection in shaping them, several studies have been carried out. Our group is contributing to achieve these aims by analysing some genetic markers in different populations from the Iberian Peninsula and South America. One of our more outstanding results shows that one of the highest frequencies of H2 subhaplotypes is found in Basque populations. Our future goals are to determine how the genetic drift and/or the natural selection have contributed to reach this noteworthy frequency and to figure out the minimum age for the H2 haplotype in Europe and in worldwide populations.

# Genomics and Health: Detection of genetic and environmental factors related with predisposition to complex diseases.

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KEY WORDS: genomics, candidate genes, gene expression, infectious diseases, obesity, eating disorders, disease resistance.

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## **HUMAN HEALTH: GENE/ENVIRONMENT INTERACTIONS**

Obesity and its associated comorbidities, represent one of the biggest public health challenges today. The marked rise in obesity observed over the last years suggests that behavioral and environmental factors underpin the mismatch between energy intake and energy expenditure. The epidemiology of obesity suggests that, for the majority of individuals, the disorder arises from an interaction between genetic predisposition and lifestyle behaviors such as dietary intake and physical activity.

Recently, dietary pattern analysis has emerged as an alternative and complementary approach to examining the relationship between diet and the risk of chronic diseases. Instead of looking at individual nutrients or foods, pattern analysis examines the effects of the overall diet. Conceptually, dietary patterns represent a broader picture of food and nutrient consumption, and may thus be more predictive of disease risk than individual foods or nutrients. Several studies have suggested that dietary patterns derived from factor or cluster analysis predict disease risk or mortality. We have detected 2-3 dietary patterns in the laboral population under study, depending on the analysis of the population as a whole or analysing males and females separately.

Our next goal will be the detection of associations between the genetic variation in some candidate genes selected from previous Genome-wide association (GWAs) studies and the obese and pre-obese phenotypes, as well as the interactions with environmental factors, including dietary patterns and other lifestyle factors.

## **ANIMAL HEALTH: HOST/VIRUS INTERACTIONS**

We are involved in the analysis of the genetic basis of infectious diseases with viral aetiology in domestic and non-model animals.

Recently, we have sought to contribute to the clarification of some aspects of the pathogenesis of two viral diseases in sheep, Ovine Pulmonary Adenocarcinoma (OPA) and Visna/Maedi by analysing a number of candidate genes of both the innate and adaptive immunity with different markers and techniques (Sequence Based Typing, Microsatellites, SNPs) and their expression in different tissues. Association analysis between markers and OPA development has led to the discovery of a number of novel genes related with disease progression, namely MX1 and CCR5. Moreover, For Visna/Maedi disease, we have performed a GWAs to detect new candidate genes, and an expression array in order to unravel the causal polymorphisms and the mechanisms with which they confer Resistance/Susceptibility to disease progression.

We are also interested in the analysis of endogenous retroviruses (ERVs), genomic elements with retroviral origin, which can have both beneficial (resistance to infectious counterparts) and adverse effects (may cause disease) in the host in different animal genomes. We have carried out a multi-species genomic analysis to identify retroviral elements inserted in these genomes by bioinformatic methods.

For OPA disease, we are conducting genomic and epigenetic studies of sheep endogenous polymorphic retroviruses, the endogenous homologues of the Jaagsiekte sheep retrovirus, the causative agent of OPA disease. We have detected and characterized retroviral elements in the sheep genome by molecular techniques such as PCR suppression and iPCR. We are now analyzing their expression in different tissues in healthy and diseased animals.

We hope that this line of research will open new channels for the elimination of infectious diseases affecting livestock and other animal species.

# Bacterial resistance to stress: fundamentals and applications

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KEY WORDS: bacteria, adverse environments, resistance.

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Microorganisms are exposed to periodic stresses and abiotic and biotic factors drive the behavior of microbial populations in those changing environments. Their adaptation capacity and their physiological plasticity allow them to survive in habitats in which the environmental conditions are not the optimal ones for life.

Our group has previously studied the response of *Escherichia coli* (intestinal bacteria) to different abiotic stressors (starvation, sub-optimal temperature, luminous irradiation, etc.) as well as its relationship with natural microbial communities (protozoa, autochthonous bacteria and bacteriophages). Those questions have been analysed via traditional methods in microbiology, new molecular methodologies, the use of strains easily identifiable into complex matrices, etc. Our results indicate that abiotic factors promote physiological and molecular response to ensure the persistence of part of the population, while biotic factors can lead to the elimination of the bacterial population.

Subsequently, we have transferred this knowledge to the study of the behaviour of *Vibrio harveyi* in aquatic environments. *Vibrio* (i.e. *V. cholerae*) has a maximum growth temperature at 28°C but it can remain in water in the cold season at 4°C, and exponentially grow again in the warm season (20°C), when the temperature increases. Moreover, with the increase in temperature that the climatic change implies, the seasonal distribution of *Vibrio* in water has been modified.

Nosocomial pathogenic bacteria as *Acinetobacter baumannii* can survive and persist in clinical environment for long periods. The understanding of the mechanisms and survival strategies of this bacterium could facilitate the control and disinfection of surfaces and risk areas.

Another field of interest of our group is the study of biological processes occurring during a wastewater treatment process by activated sludge. Wastewaters are the perfect vehicle for dissemination of faecal and other microorganisms. We study the importance of mechanisms implicated in the elimination of faecal bacteria during treatment: adhesion to flocs/sludge, elimination by grazing, parasitism, competition, etc.

Methodologies and setups used previously have been shown to be suitable to implement in these new areas of interest: the study of the effect of climate change in bacterial populations, finding new disinfection protocols, understanding water treatment processes.

The techniques and methodologies used include: epifluorescence microscopy, fluorescence *in situ* hybridization, analysis of bacterial proteome, water quality analysis, tests for disinfectants and other toxic compounds, etc.

# New approaches in genomics, transcriptomic analysis and molecular microbiology to detect *Aspergillus fumigatus* and understand its infections

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KEY WORDS: *Aspergillus fumigatus*, Pathogenesis, Genomics, Proteomics, Gene expression, Detection, Diagnosis.

*Aspergillus fumigatus* is considered to be the most prevalent airborne pathogenic fungus. Despite immunocompetent hosts do not develop illnesses, in immunocompromised patients the inhalation of its conidia can result in allergic or invasive diseases. Among them, the most severe form is invasive aspergillosis (IA) with mortality rates of 70-90%, which are mainly due to the weakened immune system of the patients, the virulence of the fungus and late diagnosis. In addition, several studies have demonstrated that the pathogenesis of this fungus is multifactorial owing to a combination of its biological characteristics and the immune status of patients.

## PURPOSE

- To improve the knowledge of the molecular factors involved in the virulence of *A. fumigatus* analyzing its transcriptome under different conditions following hybridization with the whole genome microarray designed by our group.
- To develop Real Time PCR methods that allow a quick detection of *A. fumigatus* and other pathogen species that belong to *Aspergillus* genus.
- To find out new pathways involved in the pathogenesis and virulence of this pathogen which might be useful to design new therapeutic strategies.

## TECHNIQUES

- Conventional microbiological techniques to cultivate and observe the growth features.
- DNA and RNA extraction and electrophoresis for molecular studies.
- Immunological and histological techniques.
- Sequencing and bioinformatics.
- Animal model and cell line infections.
- Gene expression analysis following the hybridization with the whole genome microarray.
- Conventional PCR, real-time PCR, multiplex PCR, and reverse transcription quantitative PCR for detection and diagnosis.

These studies could show proteins or new pathways involved in the pathogenesis and virulence of *A. fumigatus* allowing the development of new antifungal therapies. Furthermore, the identification and selection of genes that unequivocally might be related with the infection or the presence of this pathogen in patients could be used as diagnostic targets to detect the infection.

## RELATIONSHIPS

- Hospital Universitario y Politécnico La Fe. Valencia.
- Tecnalia, Vitoria-Gasteiz.

## PATENTS

- Fernandez et al. N. de solicitud: P201131497 (15/11/2011) Entidad titular: UPV/EHU.

# What can marine microbes tell us about...

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KEY WORDS: marine ecosystem, bacterial diversity, ecological function

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The relationship between bacterial community composition and activity in space and time is one of the central topics in microbial ecology. Diversity and function in microbial communities are usually related, thus variations in the structure of the microbial community are thought to play a major role in regulating the biogeochemical processes of the aquatic systems. Our main objective is to unveil the dynamics of the microbial communities in the marine environment. Among others, we study the abundance, specific composition, diversity and function of prokaryotes and bacterivorous protists.

## ... RECURRING PATTERNS OF AN ECOSYSTEM?

The Project “**Cambio. Bacterioplankton Diversity and function of the bacterioplankton in the Eastern Cantabrian Sea: Grazing and nutrients as drivers of the seasonal change**” (MICINN, CTM2010-19308/MAR) focuses on:

- The specific composition and diversity of the bacterioplanktonic community in coastal waters of the Eastern Cantabrian Sea.
- The identification of the seasonal changes in the relevant members of that community over multi-year time scale.
- The establishment of links between the taxonomic diversity and the physiological function of bacterioplankton, resulting in an optimization of available resources.
- The relevance of protistan grazing compared to other environmental factors, as a significant driver of the change of relevant members of the community.

The results obtained in this Project will allow not only to generate baselines which will be essential references in future analysis of changing environmental conditions (anthropogenic global warming, acidification, toxic wastes, etc.), but also to achieve a higher predictive capability about the performance of the ecosystem under different seasonal conditions.

## ... FLUXES OF MATTER AND ENERGY IN THE OCEAN?

The Project “**Circumnavigation Expedition Malaspina 2010; Global Change and Biodiversity Exploration of the Global Ocean**” (MICINN, CSD2008-00077) is an interdisciplinary project divided in 7 thematic blocks (The Malaspina Expedition, Heat and Mass flow, Biogeochemistry, Optics and Phytoplankton, Contaminants, Zooplankton, and Microbial Processes) and 4 transversal blocks (Dissemination, Training, Integration, and Coordination). Its main objectives are:

- To assess the impact of global change on the ocean.
- To explore the biodiversity and the functional role of the microorganisms in the biogeochemical transformations of organic matter, with special interest in the deep-sea.
- To analyze the repercussion of the expedition of Alejandro Malaspina.
- To promote marine science and knowledge in the Spanish society.
- To train and attract young researchers.

In the expedition, financed by the Spanish Ministry of Science, two research vessels were involved: the *Sarmiento de Gamboa* in the North Atlantic Ocean transect by 24 °LN, and the *BIO Hespérides* in a circumnavigation of the Earth during seven successive cruises (Cádiz-Rio de Janeiro-Cape Town-Perth-Sydney-Auckland-Honolulu-Panama-Cartagena de Indias-Cádiz).

*In situ* measurements were carried out and about 120,000 samples from water, air and plankton were taken during 2010-11 along the water column, from surface down to a depth of 4.000 meters, in 300 stations distributed through the Atlantic, Indian and Pacific Oceans.

# Post-transcriptional mechanisms in bacteria and their regulation by environmental signals

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KEY WORDS: bacterial stress responses, antisense RNAs, degradosome, glycolysis

The ubiquitous presence of microorganisms is largely associated with their unique abilities to adapt and thrive in adverse environments. We use the Gram-negative bacterium *Escherichia coli* (*E. coli*) as a model organism to study post-transcriptional mechanisms controlling mRNA stability as well as regulation of these mechanisms by environmental signals. Our two major lines of research are briefly described below.

## 1. HIGH-THROUGHPUT SCREENING AND FUNCTIONAL ANALYSIS OF ANTISENSE RNAs WITH NEW ROLES IN *ESCHERICHIA COLI* STRESS RESPONSES

Recent studies revealed a new class of small antisense RNAs (sRNAs) that play important roles in regulatory mechanisms that enable *Escherichia coli* and other bacteria (including essential genera of pathogenic enterobacteria) to adapt to environmental stresses. Analysis of several stress-related sRNAs demonstrated that they can exert their regulatory functions by basepairing with their target mRNAs to alter mRNA translation and stability in an Hfq-dependent manner.

Given important functions of sRNAs in bacterial adaptation and virulence, the main goal of our project is to employ a combination of high-throughput biochemical, genetic and molecular biology approaches and characterize a large fraction of experimentally identified and *in silico* predicted sRNAs that have not been studied previously. The specific aims of the project are to

- Characterize antisense RNAs with new roles in bacterial stress responses;
- Examine their regulatory functions using *Escherichia coli* as a model organism;
- Investigate how the formation of sRNA/mRNA complexes affect the fate of selected sRNAs and their targets, and determine the contribution of the RNA chaperone Hfq and cellular ribonucleases to the rate-limiting and subsequent steps in disassembly and processing of these complexes *in vivo*.

## 2. ANALYSIS OF PROTEIN-PROTEIN INTERACTIONS AND SUBCELLULAR LOCALIZATION OF GLYCOLYTIC ENZYMES IN *E. COLI*

Previous work has shown that the glycolytic enzyme enolase is a major component of the degradosome, a multienzyme complex controlling RNA processing and decay in *Escherichia coli* (*E. coli*) and additionally containing RNase E, PNPase (exoribonuclease) and RhlB (DEAD-box helicase). While association of RNase E with RhlB and PNPase was shown to be critical for the normal efficiency of the degradosome-mediated RNA decay, the function(s) of enolase in the degradosome remains uncertain. As ATP is an important cofactor of the degradosome, the presence of enolase in this complex suggests that the degradosome-dependent RNA turnover and the enolase-mediated ATP production (glycolysis) may be coordinated through co-localization of both processes *in vivo*.

This assumption, in turn, raises a number of fundamental questions regarding the membrane organization of the glycolytic complex, its composition and interactions with the major components of the RNA degradosome. The long-term goal of our study is to perform in-depth analysis of the protein-protein network that control glycolysis and link this process to RNA turnover and sugar transport in *E. coli*. The specific aims of the project are to:

- Identify interacting partners of glycolytic enzymes in *E. coli*;
- Reveal and validate specific protein-protein interactions involving glycolytic enzymes and their interacting partners and
- Test the contribution of these interactions to the subcellular localization and co-localization of glycolytic enzymes with the major components of the *E. coli* degradosome.

# Virulence Mechanisms of Fungal Pathogens

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KEY WORDS: *Candida albicans*, *Scedosporium prolificans*, Immunocompromised patients, Cancer, Mannoproteins, Immunoglobulins

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Our research group is interested in studying the virulence mechanisms of two fungi involved in systemic infections of immunocompromised patients. The first of them, *Candida albicans*, is a dimorphic commensal yeast that is the most prevalent fungus in health-care associated infections and is also related to inflammatory response and tumour adhesion. The second one, *Scedosporium prolificans*, is a filamentous fungus isolated from humanized environments mainly in the Iberian Peninsula and Australia, which induces high mortality rates in immunocompromised population due to its great virulence and inherent resistance to almost all antifungals

Our group has hypothesized that, in immunocompromised patients, the inflammatory response of endothelial cells stimulated by *C. albicans* may favour the adhesion of the tumour cells to these cells, leading to liver metastasis. We characterised the mannoprotein fraction that increases the tumour adhesion the most, and identified the main mannoproteins within this fraction. Then, we proceeded to produce them as recombinant proteins in a bacterial (*Escherichia coli*) and an eukaryotic model (*Pichia pastoris*) in order to obtain them individually at high concentration. Afterwards, the proteins were purified and tested *in vitro* for their pro-inflammatory and pro-metastatic effect on mouse hepatic endothelium. Some of the produced recombinant proteins were selected and monoclonal antibodies against them are being currently produced. Once obtained, the effect of these monoclonal antibodies on the viability of *Candida*, and on the inhibition of pro-inflammatory and pro-metastatic effect of the yeast will be studied. Finally, we will also study the effect of expressed recombinant proteins and the yeast directly in two tumour lines (B16 melanoma and H357 oral squamous cell carcinoma) by cell-yeast coinubation. This effect will be tested by measuring parameters such as cancer cell viability and proliferation, phagocytosis of the cancer cells over the yeast, and progression of cancer cells into a more malignant phenotype, among others.

On the other hand, we are studying the fungal pathogenesis of the filamentous fungus *Scedosporium prolificans* by applying omic technologies. As no in-depth proteomic analyses had been performed concerning this microorganism, we established a workflow for protein extraction, both from its conidiospores and hyphae. In this way, we are nowadays researching to identify proteins related to the aforementioned antifungal resistance by growing the fungus in the absence or presence of the antifungal drug. Moreover, we have recently characterized the recognition profiles of human salivary IgA against *S. prolificans* proteins and we have identified a number of antigenic proteins that may be useful as new targets for innovative therapeutic or diagnostic strategies. Finally, we are interested in describing the cell-mediated innate immune response against this fungus. To analyze that, we will use an *in vitro* infection model using the ANA-1 macrophage cell line to determine cytokine and ROS production, which receptors and mechanisms are involved in cell-fungus interactions, etc. Moreover, as *S. prolificans* has been described as neurotropic when it gets disseminated into the host, we will study how these infections evolve by using infection models with the microglial cell line BV2 and whole brain organotypic cultures.

This work has been supported by two SAIOTEK grants (S-PE12UN075 and SAI13/116), a grant for Young Researchers EHUA13/14, and an UFI Grant (UFI11/25) from UPV/EHU. AP and JVF are supported by UPV/EHU FPI fellowships, and AA and MS are supported by Basque Government FPI fellowships.

# The wonderful nano world: are there any risks for the environment?

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KEY WORDS: metal nanoparticles, toxicity and mechanisms of action, alternative methods, mussel, zebrafish, earthworm, environmental risk assessment.

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In order to assess the potential toxicity of metal nanoparticles (NPs) and to elucidate the mechanisms of action of these emerging contaminants in aquatic and terrestrial animals, an integrated methodology in which alternative toxicity testing methods have special relevance has been designed. We evaluate the toxicity of metal NPs in comparison with the ionic and bulk forms and, if present in the formulation, with the stabilising or surfactant additives. For this purpose, we employ different experimental approaches in three model organisms:

1. *In vivo* exposure of mussels *Mytilus galloprovincialis* and *in vitro* exposure of mussel cells. Mussels, as an invertebrate species, are considered an alternative experimental model. Filter-feeding bivalves are potentially a target species of nanomaterials entering the water column and, thus, they are suitable sentinel species to monitor NP impact into the marine and estuarine environment. Mussel haemocytes and gill cells are being used as representatives of the internal defence system and of epithelial cells in direct contact with water pollutants.
2. *In vivo* exposure of zebrafish *Danio rerio*. Zebrafish is a consolidated experimental model in biomedicine. In this case, zebrafish are being exposed at two developmental stages: newly fertilised embryos up to the end of organogenesis (5 days) and juvenile-adult zebrafish.
3. *In vivo* exposure of earthworms *Eisenia fetida* and *in vitro* exposure of coelomocytes. Earthworms are terrestrial model organisms that have been widely used as bioindicators of soil pollution and have been prescribed as a test organism for standard toxicity tests (OECD, ISO) due to its sensitivity and easy maintenance.

In the three cases, a two-tier procedure is employed. In the first tier, NPs at a wide range of concentrations depending on the expected toxicity are tested using different screening methods: short-term *in vivo* exposure of adult mussels, zebrafish embryos and earthworms or *in vitro* tests with mussel cells and coelomocytes from earthworms to detect direct cytotoxicity. Based on the results of these screening experiments, LC50 values are calculated and sublethal concentrations of NPs, bulk and ionic forms are selected for in-deep mechanistic studies. In the second tier, longer-term exposures are carried out with mussels, adult zebrafish and earthworms and a set of toxicity and bioaccumulation endpoints are assessed, as well as changes in the gene expression patterns using microarrays, while a battery of mechanistic assays are performed in the primary cell cultures.

All results obtained up to date indicate that ionic forms are more toxic than nanoparticles and the latter are more toxic than their corresponding bulk forms. Ag NPs resulted the most toxic of metal NPs tested up to date (ranking of toxicity: Ag > Cu > Cd > ZnO > Ti > Au > Si). Some additives present in NP formulations show also significant toxicity and thus need to be considered in environmental risk assessment of NPs. Our work is contributing to decipher the mechanisms of action of metal NPs at cellular and molecular levels. In general, organisms use the same pathways to respond to NPs as to the corresponding ionic forms but NP-specific effects have also been identified.

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# Sex determination and differentiation in fish: environmental effects and biotechnological applications

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KEY WORDS: palabra uno, palabra dos, palabra tres.

Early studies performed by the research group Cell Biology in Environmental Toxicology, both in the laboratory and in different Basque estuaries, have demonstrated the potential of environmental pollutants to affect the reproductive ability of aquatic organisms, mainly fish. Effects on reproduction could be the result of a variety of toxicity mechanisms operating first at the molecular level. Notably, the presence of some chemicals in the aquatic environment, termed endocrine disrupting chemicals (EDCs), the increase in water temperature or changes in the availability of O<sub>2</sub> and food can cause adverse effects on growth, behavior and reproduction by interfering with the endocrine system. In some cases, these molecular mechanisms lead to the feminization of exposed fish populations, male fish developing oocytes in testis (intersex condition). Within the project SEXOVUM we are trying to develop molecular markers to identify early feminization responses in fish populations, studying some mechanisms that regulate fish gonad differentiation under exposure to xenoestrogenic EDCs. We are specifically studying the mechanisms that regulate accumulation of ribosomal intermediates in oocytes, and the way in which they can be used in environmental health assessment, fisheries research and aquaculture.

We use widely acknowledged molecular biomarkers of xenoestrogenic exposure, such as up-regulation of gonadal and brain aromatases and hepatic vitellogenin at transcription or protein level in male thicklip grey mullets (*Chelon labrosus*), in field scenarios in the Basque coast. This allows monitoring the health status of our littoral waters in relation to the presence of EDCs. We have additionally developed a series of molecular markers for the identification of oocytes in gonads, both in ovary or in intersex testis. A simple electrophoresis of total RNA extracted from the gonad of mullets allows identification of a strong expression of 5S rRNA in oocytes. Oocytes need to accumulate 5S rRNA in order to quickly assemble ribosomes in case of being fertilized. This allows sustaining protein synthesis during embryogenesis. In the same way, transcription factors for 5S rRNA expression (TFIIIA), proteins for 5S rRNA cytoplasmic stockpiling (TFIIIA and 42sp43) and proteins for nucleocytoplasmic transport of proteins/ribonucleoproteins are strongly transcribed in oocytes and not in somatic cells or in the spermatogenic line. The use of these oocyte markers to sex mullets and identify intersex mullets has been patented.

The use of 5S rRNA and TFIIIA as molecular markers for the identification of sex in teleost fish has been proved in many fish species of commercial/scientific interest (megrim, European hake, anchovy, pilchard, sea bass, blue whiting, different mackerels, zebrafish). Further, a 5S/18S rRNA index has been developed that additionally allows classifying females according to their maturation and gametogenic stage. This knowledge can be used as a method to analyze fish stock dynamics, classifying populations in stock managing research campaigns according to their sex distribution and maturity stage.

Still 5S rRNA analysis in gonads can find applications in aquaculture. If 5S rRNA is accumulated during oocyte development to sustain embryo development, the levels of accumulation might predict the quality of the eggs and the reproducing females. For this purpose, in collaboration with the Galician Aquaculture Cluster we are following the reproductive performance of 15 female turbot, fertilized with the sperm of a single male. Levels of 5S rRNA present in the eggs are being studied with the intention to correlate them with the performance of the progeny of each female (fertilization success, hatching rate, survival rate, size dispersion).

All these applied research studies are being conducted together with more basic research studies that try to understand the mechanisms regulating differential expression of 5S rRNA in testis and ovary during sex determination and differentiation.

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# Entomology applied to Forensic Research.

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KEY WORDS: Entomología forense, Artrópodos, Desarrollo. Distribución, Sucesión faunística, Genotipado, ADN.

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## 1.- Concept

Forensic Entomology applies the knowledge about the structure and dynamics of insect and other arthropods to assist in legal matters resolution, such as judicial (abuses, neglect, crimes o deaths) or economic problems (infestations or plagues), where the correct interpretation of the information provided by entomologic evidences can play a valuable or even crucial role, particularly, in Court proceedings.

## 2.- Applications

1. Evaluation of the insect activity (PIA) in a sample to estimate
  - a. Postmortem Interval (PMI) in cases of murder, suicide or natural death.
  - b. Data, origin and type of contamination, abuses o neglects involved in myiasis of animals and dependent people (sick or elderly people and children), infestation of stored food, real property and other legal aspects.
2. Detection of toxics and/or drugs in corpse remains; bioaccumulation of chemical metabolites such as drugs in corpses and other remains.
3. Molecular identification of human cadavers, based on gut contents from entomological evidences.
4. Maggot therapy; larvae activity of some species can remove only the necrotic tissues and promote wounds healing.
5. Illegal traffic; the use of insects as geographic indicators provide information to solve illegal traffic of vehicles and goods deal.
6. Identification and estimation of damages to personal and other kind of properties.
7. Population control, to prevent sanitary and economics problems that some insects can cause (pest, disease vector, etc.)
8. Organic waste treatment, as the high metabolic activity of necrophagous species can be useful to reduce organic residues of animal origin.

## 3.- Main Objectives that are being developed by the research group

1. To ensure common guidelines and standard protocols for best practice in forensic entomology that guarantee the collaboration with forensic pathologists and police.
2. To increase our knowledge about the necrophagous fauna in C.A.P.V.:
  - a) Morphological identification of the main infesting species.
  - b) Molecular tipification of the most relevant entomofauna for forensic purposes.
  - c) Estimate their developmental rates in our latitudes.
  - d) Establish the faunal succession patterns on cadavers in our biogeographical environment.
  - e) Use of parasitoids in pest control
3. To develop different control strategies for the insect populations that cause damages in transported or stored feed, cattle, areal properties and other material damages.
4. To apply knowledge about developmental biology of necrophagous species suitable to an efficient waste management as a possible tool to reduce residues organic fraction.

# Traceability of changes in biomarkers depending upon sampling conditions

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KEY WORDS: sampling strategy, biomonitoring, biomarkers, *Mytilus galloprovincialis*.

In order to harmonize assessment and monitoring procedures for implementing the European Marine Strategy Framework Directive (MSFD) in the Bay of Biscay, one of the main objective of the project untitled “Towards science-based standard biomarker methods, suitable to diagnose and monitor pollution biological effects in the Bay of Biscay for the purpose of implementing the European Marine Strategy Framework Directive”(MINECO 2013-2015) is to optimize existing biomarker methods for mussels by reducing variability and improving sampling, processing and analytical procedures. With this aim, and knowing that there are differences on the collection and pre-processing strategies of mussels between different research teams working on assessment and monitoring programmes, and in order to advance in the understanding of biomarkers variability and responsiveness depending upon sampling strategies, the present study was carried out. Mussels *Mytilus galloprovincialis* were collected from Gortiz, a reference locality of the Basque Coast, in September 2010. Low and high intertidal mussels were handpicked and they were pre-processed differently: *in situ*; transported in air to the laboratory and sacrificed 3 hours after sampling; transported and maintained in water and sacrificed 3 and 24 hour after sampling. Accordingly, a battery of biochemical (glutathione S-transferase (GST); catalase (CAT), glutathione peroxidase (GPx), glutathione reductase (GR); levels of lipids peroxides (LPO); and cholinesterase (ChE)) and cell-level (labilization period of lysosomal membrane (LP); lysosomal enlargement (VvL) biomarkers was measured. Biochemical biomarkers showed higher ChE, GST and GR activities and lower LPO and GPx activities when mussels were pre-processed *in situ*. Although no significant, differences were recorded on lysosomal biomarkers among sampling strategies, LP values trends to be lower and VvL values trends to be higher in mussels pre-processed *in situ*. Overall, the obtained results demonstrate that the sampling strategies could influence on biomarkers. But we must be conscious that we are assessing the environmental health by taking into account a particular moment. Thus, it is concluded that sampling protocols are needed in order to avoid as much as possible natural variability on biomarkers and differences produce in the manipulation of samples.

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# Fisika eta Ingeniaritza Elektronikoa



Física e  
Ingeniería Electrónica

# Software Technologies Working Group (GTTS, <http://gtts.ehu.es>)

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KEY WORDS: Information Retrieval for Multimedia Resources, Language and Speaker Recognition/Verification, Automatic Speech Transcription, Automatic Video Subtitling/Captioning

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Research at GTTS focuses on fundamental software technologies, in particular those related to speech processing and information retrieval. We are working on speech segmentation, language and speaker recognition/verification, speaker diarization, automatic speech transcription, video subtitling, etc. Part of our efforts are devoted to develop tools and prototypes for various applications:

1. A spoken document retrieval system (Hearch: <http://gtts.ehu.es/Hearch/>) which looks like a conventional search tool (such as Google, Bing, etc) but is designed to retrieve audio/video segments based on the automatic transcription of speech contents (broadcast news repositories in Spanish and Basque, plenary sessions of the Basque Parliament, etc.).
2. An automatic bilingual video subtitling system applied on the plenary sessions videos that the Basque Parliament posts in its website (<http://www.parlamentovasco.euskolegebiltzarra.org/>), running from September 2010.

Finally, we also devote great efforts to academic training (master projects and doctoral theses), dissemination of results (both in prestigious publications and through technology transfer to companies in our area) and collaboration with other research groups.

## ACTIVE PROJECTS

- Saiotek (Basque Government), (S-PE13UN105): Verificación de identidades mediante la huella vocal en aplicaciones de alta seguridad (PASAHOTTS).
- University-Society (UPV/EHU and Basque parliament) (US11/06): Search platform of multimedia contents for business and scientific exploitation.

## RESEARCH ACTIVITY IN THE LAST FIVE YEARS

- UPV/EHU Research Group: 2013-2016 (37.000 euro)
- Projects, contracts and research fellowships: 10 (320.000 euro)
- Publications: 45 (4 journals, 41 peer-reviewed conferences)
- Thesis: 1 presented and 3 in progress
- Participation in international evaluations:
  1. NIST Language Recognition Evaluation (2007, 2009 and 2011)
  2. NIST Speaker Recognition Evaluation (2008, 2010 and 2012)
  3. NIST Open Keyword Search Evaluation (2013)
- Organization of international evaluations:
  1. Albayzin Language Recognition Evaluation (2008, 2010 and 2012)
  2. MediaEval Benchmarking Initiative for Multimedial Evaluation: The Spoken Web Search Task (2013)

## TECHNOLOGY TRANSFER

- Hitzaldi: tool for audio-text alignment in parliamentary sessions.
- Sautrela: software package (free access) for the development of speech processing applications.
- Hearch: search tool for audiovisual resources (from automatic transcriptions of speech).
- Kalaka, Kalaka-2 and Kalaka-3: databases for the development of language recognition systems.
- ICT-COST 278: database of TV news in Spanish and Basque for audio segmentation and speaker diarization.

# Plasmonics of metallic nanoparticles linked by molecular structures: optical and transport properties

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KEY WORDS: nanophotonics, plasmon resonances, molecular linkers

We study theoretically the electromagnetic response of metallic nanostructures, free-standing or supported on surfaces, when they are excited by external sources such as electron beams (electron microscopy) or light (optical spectroscopy). In both cases, resonant oscillations of free electrons, called plasmons, emerge in the nanostructures. From a basic research perspective, these systems are very interesting since their optical properties differ from the optical response of the same metallic material in the bulk. On the other side, these systems are the basis for applications such as sensing, surface-enhanced spectroscopies, cancer therapies, renewable energies or active devices.

In particular, we have studied the relation between the optical properties and the transport properties of a hybrid nanostructure consisting of a chemically synthesized metallic nanoparticle dimer connected by a molecular structure. Our goal is to achieve a better understanding of the complex connection between the electronic transport through molecular linkers and the changes in the optical extinction spectra of the connected dimers in the visible and near infrared frequencies.

The molecular linker connecting the dimer has been modelled with increasing complexity. First, it has been considered as a cylinder with a purely conductive nature, which helps to understand the main spectral trends of the emerging plasmon modes [1,2]. In a second step, a more realistic dielectric response of the linker has been considered, taking into account the excitations of the connecting molecules. This leads to a more complex optical response involving the interaction of the plasmon cavity modes and the excitons from the molecular transitions [3]. Finally, the possibility of an ensemble of molecules entirely covering the nanostructure is considered as well [4]. In comparison to the case when the molecules are placed only in the interparticle gap, for the entirely covered dimer a new resonance emerges, arising from the interaction of the plasmon cavity modes and the geometrical modes of the molecular aggregate shell.

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# IZPILab: RF and Control Applications for Particle Accelerators

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KEY WORDS: RF instrumentation and control, beam diagnostics, particle accelerators, EPICS.

Researchers from the RF and Microwaves, and the Automatic Control Group of the Department of Electricity and Electronics have founded IZPILab, a joint Beam Laboratory for the development of Electronics, RF and Control Applications for Particle Accelerators, including beam generation, beam transport and beam measurement and diagnostics. The research activities refer to problems, both from basic science and from applied science and technology in the field of Particle Accelerators, where RF and control play a relevant role. Current projects include the development of beam sources, beam diagnostics, RF devices and controls, and the corresponding electronics.

## EPICS AND DISTRIBUTED CONTROL SYSTEMS

EPICS (Experimental Physics and Industrial Control System) is a set of Open Source software tools, libraries and applications developed collaboratively and used worldwide to create distributed soft real-time control systems for

scientific instruments such as a particle accelerators, telescopes and other large scientific experiments. Goals of the group using EPICS:

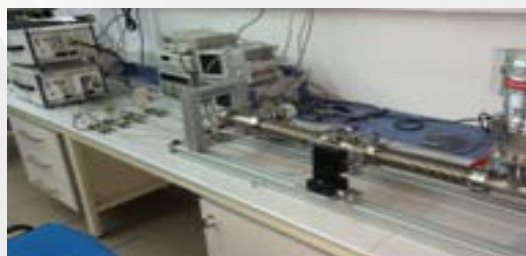
- To integrate modern control standards in a single system for scientific facilities together with usual automatic control tools.
- To develop this middleware to get an efficient and secure communication between all devices, redistributing messages and requests.
- To compare different EPICS developments and solutions, using hardware test-benches.
- Integration into an EPICS net of some common diagnostics and control devices (BPMs, LLRF) widespread in Particle Accelerators.

The research group has started a collaboration with the research center Centro de Laseres Pulsados UltraCortos Ultraintensos (CLPU) of Salamanca for development and integration of EPICS networks.

## PARTICLE ACCELERATOR SCIENCE AND TECHNOLOGY

The group is involved in several projects for particle accelerators. Among these it is worth mentioning:

- Beam diagnostics and related electronics: active projects are related with Beam Position Monitors, for highaccuracy measurement of beam bunches position; Integration between EPICS and the RF Cavities control system; Beam profile diagnostics based on secondary electron emission.



- Beam generation through compact new generation microwave-driven ion sources.
- RF Instrumentation and Control: In an RF accelerator, the particles are accelerated by RF fields with appropriate amplitude and phase, through a high power transmission chain comprising a wide range of control systems. The research group is working on:

1. Low-Level RF controls of frequency, amplitude and phase of accelerating RF signals injected into the particle accelerating structures and to get linear and spurious-free behavior of RF transmitters
2. RF subsystems to optimize RF signal injection in RF cavities for plasma generation or particle acceleration
3. Experimental characterization and conditioning of low and high power RF devices and subsystems

# Grupo de Investigación en Automática Experimental GAUDEE

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KEY WORDS: Control, actuators, smart materials, sensors

The Automatic Control Group of the department of Electricity and Electronics, GAUDEE, is a group of teachers and researchers mainly in the field of Systems Engineering and Automatic Control that focus on the development and application of advanced control techniques, combining both basic science and applied science and technology. The group is mainly interested in solving questions of possible importance in production or industrial processes. It is involved in several research projects like smart materials, event control techniques and high resolution sensors based on new principles.

## DESIGN OF NEW ACTUATORS AND PRECISION SENSORS EVENT-BASED CONTROL

Smart materials are capable of responding, in a controlled fashion, to one or more different external stimuli. External stimuli can be physical or chemical, like magnetic or electric fields, and the response can, for example, be a change in dimensions. A large field of application of these materials is as sensors or actuators, especially when trying to improve their performance.

Ferromagnetic shape memory alloys (FSMAs) are a particular example of smart materials. They exhibit large strains (~6%) under applied magnetic fields, meaning they don't need to be directly contacted to be actuated. However, the hysteretic nature of the material presents a challenge to the control of the material, and requires a purpose-built controller.

From this line of research, we propose a new actuator based on two orthogonal fields. So far, very encouraging results have been obtained and positioning accuracies on the order of nanometers are achieved with the advantage of substantial energy saving.

A new line of research for the group is the development of new high-resolution precision sensors based on high frequency resonant cavities. A transducer inducing resonant frequency changes as a result of positioning changes has been designed and tested, and laboratory prototypes, with proven sub-nanometric resolution, have been built. Moreover, we are now interested on developing compact and cheap electronic interfaces to these transducers, so that new high-performance standalone positioning sensors are developed.

## EVENT-BASED CONTROL

Event based control allows the optimization of system resources reducing the number of control actions.

The research group works in the development of new schemes using this technique in order to obtain a energy consumption reduction and a minimization of the actuator usage, leading a lower maintaining cost. Using eventtriggered sampling, a quantized set of possible sampling times is defined, facilitating the implementability of the proposed schemes.

## MODELING, CALIBRATION, DETECTION AND CONTROL OF CHATTER

As member of the European DYNEXPERTS project, the group has been working in the development and test of different techniques for the modeling, analysis and control of chatter in machine tool systems. Among others, an active magnetic bearing levitated head for high speed machining has been under study.



In the analysis and control of chatter is important the use of active vibration control techniques. During the cutting process in turning or milling applications, the vibrations can lead to a regeneration effect, called chatter, which deteriorates the resulting mechanical piece. To prevent this effect, different devices to increase the damping has been developed and tested.

These devices are usually attached to the machine head. However, in the case of the AMB based systems, the elements performing the levitation act also as damper actuators.



# RF and Microwave Group

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KEY WORDS: high frequency electronics, power amplifiers, noise characterization, radio-communication systems.

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The group works in the field of high frequency circuits and systems for different applications: wireless communications, radio navigation and scientific equipment. Our basic research axes are focused on the analysis and design of microwave circuits and high frequency instrumentation.

The increasing complexity of communication signals impose a severe R&D effort focused on new device technologies, new design techniques, advanced analysis and simulation strategies and innovative and rigorous experimental characterizations. In particular, power amplification is currently one of the main bottlenecks to achieve the strict performances of RF transmitters for modern applications. Power amplifiers are, in a great extend, the main responsible for DC consumption of the transmitter and for signal intermodulation distortion. Consequently, power amplifier design is a critical step that has to be carefully studied as a function of the application in order to obtain an acceptable compromise between linearity and efficiency. Our group has developed an extensive work on analysis and characterization of power amplifiers, including circuit linearization, circuit modeling and system simulation. We maintain fruitful cooperation with other laboratories and international institutions. As an example, we can mention the advancements on spurious oscillation detection in power amplifiers for satellite communications achieved in the framework of a project funded by the French Space Agency (CNES, Toulouse, France) in cooperation with Thales Alenia Space (TAS-F). Our group has also a relevant activity in noise characterization of RF circuits and systems, where it is worth mentioning the development of novel techniques for the amplitude noise and phase-noise measurement in the presence of large-signal excitations. We also develop today intense activity on RF instrumentation for particle linear accelerators (LINACs). As an example we can mention the development of an automatic system for impedance matching of the ESS-Bilbao protons source. Finally, we have a growing activity in RF and microwave sensors. A sub-nanometer position sensor based on resonant cavity has been recently designed and built.

# Complex system modelling and development on reconfigurable devices (FPGA) for real-time applications

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KEY WORDS: digital electronics, system modelling, embedded systems, field-programmable gate arrays (FPGAs), computational intelligence, intelligent environments, internet of things (IoT), sensor networks

The Digital Electronics Design Group (GDED) devotes its research to two main lines that converge in the development of innovative multidisciplinary applications. These lines and their application areas are:

- 1. Design of adaptive systems on a chip (SoCs) on reconfigurable devices (FPGA) for real-time applications:** hardware/software co-design, high computational efficiency hardware accelerators, device consumption and size reduction techniques, dynamic partial reconfiguration, "hardware-in-the-loop" cosimulation.
- 2. Modelling of complex dynamic systems:** computational intelligence (neural networks, neuro-fuzzy systems, and regression and optimization techniques), data mining, function approximation by means of PWL (piecewise linear) and PWM (piecewise multi-linear) techniques.
- 3. Application areas:** ambient intelligence, intelligent agents on a chip, wireless sensor networks (WSN), environmental and physiological sensors, human activity recognition and wearable computing, advanced driver assistance systems (ADAS), optimum and predictive controllers, and modelling and optimization of industrial processes (energy co-generation).

## RECENT APPLICATIONS DEVELOPED BY THE GROUP AND WORK IN PROGRESS

Intelligent environments (IE) should be able to capture and process information from multiple sensors using embedded electronic systems capable of responding in real-time. The complexity and high dimensionality of these electronic environments lead to consider simplifying elements, both in modelling and in their synthesis, with the aim of improving their efficiency and performance. The group has reported the development of a singlechip electronic device, based on reconfigurable hardware (FPGAs), which autonomously acts on IE anticipating user preferences and needs. It is a self-organizing system, without reliance on a central processor, suitable for integration into a network of autonomous cooperative devices. This is a key feature toward the integration of the system into the *Internet of Things*, a new trend in the context of ubiquitous computing and ambient intelligence.

The automotive sector has taken advantage of FPGAs, mainly due to the high computational demands of this sector where a huge amount of signals have to be processed in "real time" by means of very fast electronic systems. Present objectives of GDED include the development of embedded electronic systems, based on FPGAs, for in-vehicle deployment of ambient intelligence with the aim of improving driver performance and safety in an unobtrusive manner. The availability of advanced driver assistance systems (ADAS), inspired in safety and wellbeing, is becoming increasingly important to avoid traffic accidents caused by fatigue, stress, distractions or chronic diseases, especially since the driving population is getting older.

Finally, part of the group participates in an industrial project with several companies. The main objective of the project consists in using computational intelligence techniques for modelling the behaviour of a co-generation plant with the aim of improving its efficiency.

# Thin-film microsensors based on giant Magneto-Impedance

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KEY WORDS: Magneto-Impedance, Thin-Films and Sensors

## INTRODUCTION

The Magneto-Impedance (MI) is the change of the electrical impedance of a soft magnetic conductor when a magnetic field is applied. This is an extremely sensitive effect than can be used for developing low field magnetic sensors, with resolutions down to the pT range [1]. Thin film-based structures are preferred over wires and ribbons because can also be fabricated using standard techniques of the microelectronic industry [2]. For achieving a useful MI response, the magnetic film has to be rather thick (about 1  $\mu\text{m}$  for frequencies of 1 GHz). However, in sputtered Permalloy (Py) films, the magnetic softness is deteriorated when thick films (over 200 nm) are deposited due to the appearance of the “transcritical state”. To overcome this issue multilayered structures were developed by stacking several Py films below the critical thickness, separated by thin Ti spacers intended to interrupt the “transcritical state”. Additionally, it is possible to increase the MI performance using sandwich structures where a non-magnetic conducting layer placed between two magnetic layers. The research to optimize the properties of the materials and to develop an optimum multilayered sandwiched (MS) structure is described elsewhere [3].

## EXPERIMENTAL

Micro-shaped GMI elements have been prepared by sputtering with a multilayered and sandwiched structure, and patterned by lift-off in the form of stripes with different lengths (0.5 to 2.0 mm) and widths (70-130  $\mu\text{m}$ ). A second photolithography process defines contacts at the ends of the samples so they can be inserted in a microstrip line. Its magneto-impedance has been measured as function of the applied magnetic field (up to 150 Oe) and the frequency (up to 300 MHz) using a network analyzer. Also a dedicated electronic circuit with different detectors and MI elements has been tested and measured its noise level to determine the minimum magnetic field that can be detected.

## RESULTS AND DISCUSION

A maximum value of 150 % for the magnitude of the MI and 60 %/Oe of the sensitivity to the applied field has been found for the sample 110  $\mu\text{m}$  thick and 1 mm long. Both figures of merit strongly depend on the aspect ratio of the sample through the magnitude of the effective anisotropy [4], the quality of the patterning, and the distribution of current in the sample. The evaluation of the performance of the microsensors is completed with noise analysis. After proper matching of the MI sample in the electronic circuit, white noise values of about 120 pT/ Hz<sup>1/2</sup> are obtained.

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# Pattern Recognition and Speech Technologies

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**KEY WORDS:** Pattern, recognition, speech technologies, interactive systems.

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The group is devoted to the research and technological development in areas related to pattern recognition and speech and language technologies.

We are also aimed to advise PhD students, to train technical experts and to transfer technology to companies. Our methodological framework is the Statistical and Syntactic pattern recognition, specifically the Stochastic Finite State Automata and Transducers. Actual main research lines include: a) Spoken dialog systems: statistical approaches b) Speech recognition, understanding and generation in multilingual frameworks. c) Emotion analysis in spoken dialogs and social media dialogs. d) Machine translation for limited domains. Speech to speech translation. Specific development for Spanish and Basque.

We also strengthen potential applications such as smart man-machine interfaces for real users, automatic dialog generation for videos, serious games, dialog analysis in social media, etc

# Temperature memory effect in a multistage martensitic transformation of TiNi alloy.

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KEY WORDS: Shape memory alloys, Phase Transformations, Calorimetry, Transmission Electron Microscopy.

The research group on Physical Metallurgy and Phase Transformations (GIMF) is considered as a Consolidated Research Group A from the Basque Government, with three main research lines:

1. **Shape Memory Alloys (SMA):** Shape memory alloys are considered as smart materials because of the shape memory and superelastic properties, and are used as sensor and actuators in many industrial sectors. We elaborate polycrystals and singlecrystals of several Cu-based SMA for intermediate temperature applications (-100°C to 200°C), in particular Cu-Al-Ni and Cu-Al-Be. A complete microstructural and thermomechanical characterization is being performed in order to develop alloys for practical applications.
2. **High Temperature Intermetallics:** Intermetallic Aluminides are being developed as the new material's generation to be used in engines for aeronautic. Our interest is focused on the mobility of defects which control the deformation of these materials at high temperature, but the approach is through the study of the relaxation processes, having place in the temperature range of interest, by mechanical spectroscopy complemented by electron microscopy. At present we are working on Fe-Al and Ti-Al alloys.
3. **SMA for MEMS:** Shape memory alloys offer the highest work-output in comparison with other functional materials, and are seriously considered to work as sensors and actuators in Micro Electro-Mechanical Systems (MEMS). We approached an ambitious study on the behaviour of SMA at micro and nano scale, and we showed that Cu-Al-Ni exhibit excellent properties at micro-nano scale. We are pioneers in this field and discovered a size-effect on the superelastic behaviour.

## INVESTIGATIONS IN TiNi ALLOYS

We present in this Poster one of the recent investigations in TiNi alloys (SMA).

DSC Calorimetric measurements and in-situ Transmission Electron Microscopy (TEM) have been performed in a polycrystalline TiNi shape memory alloy (49.7 at% Ti - 50.3 at.%Ni). After thermal treatment (950°C+Ice Quenching+400°C+Ice Quenching), the TiNi wires present the characteristic multi-stage martensitic transformation (MT). TEM results show the phase sequence: R-phase (trigonal) ↔ austenitic phase (cubic B2). No martensite (monoclinic B19') phase is present. They agree with the MT stages found in DSC curves. In addition, the Temperature Memory Effect (TME) shown by shape memory alloys, has also been studied. This effect is characterized by the shift of the martensitic transformation up to higher temperatures after partial transformation cycles ("Hammer" effect). As a consequence, additional peaks are found in the calorimetric curves. Thermodynamic models based on the martensitic variant elastic relaxation during the re-nucleation processes have been proposed to explain the observed behavior.

# Copper Based Shape Memory Alloys: From Macroscopic Properties to Nano-Scale Behavior

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KEY WORDS: Shape memory alloys, Phase Transformations, Calorimetry.

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## COPPER BASED SHAPE MEMORY ALLOYS

The selected topic for the Poster is the recent investigations in Cu-based SMA.

Copper based shape memory alloys (SMA) are being developed as an alternative to the conventional Ti-Ni binary alloys because they can exhibit higher transformation temperatures, a large superelastic window, small thermal hysteresis as well as high damping coefficient and is especially noteworthy the good reproducible behaviour exhibited at nanoscale. For technological applications, low and medium temperature, specially between 100°C-200°C is of special interest.

# The Bilbao Crystallographic Server: New Databases and Tools

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KEY WORDS: Crystallographic Symmetry, Phase Transitions, Online Tools.

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The *Bilbao Crystallographic Server* (<http://www.cryst.ehu.es>) website offers crystallographic databases and programs. It can be used free of charge from any computer with a web browser via Internet. The server has been operating for more than ten years, and new programs and applications are constantly being developed. The aim of the present contribution is to report on the current state of the server.

The server is built on a core of databases and contains different shells. The set of databases includes data from *International Tables of Crystallography*, Vol. A: *Space-group symmetry*, and the data of maximal subgroups of space groups as listed in *International Tables for Crystallography*, Vol. A1: *Symmetry relations between space groups*. There is an access to the crystallographic data for the subperiodic layer and rod groups. A k-vector database with Brillouin zone figures and classification tables of the k-vectors for space groups is also available. Very recently, the Magnetic Space Groups data with general positions and Wyckoff positions for both the OG and BNS notations, along with systematic extinction rules have also been incorporated into the server and a new shell has been dedicated to the related tools (MGENPOS, MWYCKPOS, MAGNEXT, MAXMAGN).

Parallel to the crystallographic software we develop programs facilitating the study of specific problems related to solid state physics and structural chemistry. The program PSEUDO performs an evaluation of the pseudosymmetry of a given structure with respect to supergroups of its space group. The program AMPLIMODES performs the symmetry-mode analysis of any distorted structure of displacive type.

A set of structure utilities has been included for various applications such as: the transformation of unit cells or complete structures; strain tensor calculation, assignment of Wyckoff Positions. One of the newest tool called COMPSTRU is able to compare two structure descriptions characterizing the similarity of the structures models by different quantitative descriptions. It is a useful tool for the classification of structures with different composition into structure types and to determine if two structures of the same compound correspond to different phases of the same structure or if the differences are due to different measuring conditions.

Recently a new shell of computer tools dedicated to infrared absorption, Raman and hyper-Raman scattering processes was developed to study different types of programs: hyper-Raman selection rules, polarization selection rules, the behavior of the spectra under a symmetry break, etc. Applying the programs available in this shell one can calculate the resonance Raman selection rules to the study of relaxors ferroelectrics.

Summarizing, the tools located on the server can be combined to analyze, calculate and visualize problems of structural and mathematical crystallography, providing a collection of applications under the same working environment.

Geologia



Geología



# HAREA: Coastal Geology research group

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KEY WORDS: Atlantic coast, environmental transformation, natural processes, anthropogenic impact, sea-level changes

The Coastal Geology research group ([www.ehu.es/harea-geologicalitoral](http://www.ehu.es/harea-geologicalitoral)) develops a multidisciplinary approach (sedimentology, geochemistry, micropalaeontology, topography, radiometric chronology) to characterize natural and anthropogenic processes responsible for the environmental transformation of the coastal zone during the last climate cycle (Holocene and Anthropocene). Its different activities can be summarized into the following research lines and recent publications:

- 1. Environmental transformation of polluted and regenerated ecosystems.** The coastal area has experienced an intense human pressure that provoked its continuous physical destruction and a deep chemical and biological transformation. The development of environmental conservation and regeneration schemes on particular ecosystems makes necessary to carry out geological studies in order to evaluate their modern characteristics, their historical alteration processes, and the feasibility of environmental improvement proposals/ Leorri, E.; Cearreta, A.; García-Artola, A.; Irabien, M.J. y Masque, P. 2012. Recent environmental evolution of regenerated salt marshes in the southern Bay of Biscay: anthropogenic evidences in their sedimentary record, *Journal of Marine Systems* 109-110, 203-212
- 2. Sea-level variations as a consequence of anthropogenic climate change.** An increase in sea-level rise rate is potentially one of the most devastating impacts of the future climate change on the coastal areas. Climate change influences the coastline at decadal and centennial scales, and these variations of the relative sea level are registered in the coastal sedimentary sequences. The combined study of historical records and high resolution geological reconstructions of the relative sea level is a powerful tool/ Leorri, E.; Cearreta, A. y Milne, G. 2012. Field observations and modelling of Holocene sea-level changes in the southern Bay of Biscay: implication for understanding current rates of relative sea-level change and vertical land motion along the Atlantic coast of SW Europe, *Quaternary Science Reviews* 42, 59-73.
- 3. Holocene environmental evolution due to natural processes.** Due to the frequent, rapid and intense climate changes that characterize the late Quaternary period, coastal environments have experienced dramatic variations and contain a very complete record of the processes and events occurred during this time interval. The high-resolution multiproxy study of this sedimentary record allows to reconstruct the past features, to understand the present conditions and to deduce the possible future environmental variability/ Leorri, E., Drago, T., Fatela, F., Bradley, S., Moreno, J. y Cearreta, A. 2013. Late Glacial and Holocene coastal evolution in the Minho estuary (N. Portugal) Implications for understanding sea-level changes in Atlantic Iberia. *The Holocene* 23, 353-363.
- 4. Sedimentary processes with social and economic consequences.** Sedimentary processes in the estuarine areas are frequently altered by man-induced activities which can lead to undesirable repercussions. Sedimentological studies contribute to understand the role of humans and to establish suitable strategies for sustainable development/ Monge, M., Cearreta, A. y Evans, G. 2013. Morphodynamic consequences of dredging/dumping activities along the lower Oka estuary (Urdaibai Biosphere Reserve, southeastern Bay of Biscay, Spain), *Ocean and Coastal Management* 77, 40-49.
- 5. Geological assessment of archaeological deposits.** Human exploitation of natural resources has left a significant footprint in the environment since ancient times. Evaluation of pollution levels and ecological impacts derived from these historical activities in archaeological deposits is possible/ Irabien, M.J.; Cearreta, A. y Urteaga, M. 2012. Historical signature of Roman mining activities in the Bidasoa estuary (Basque Country, northern Spain): an integrated micropalaeontological, geochemical and archaeological approach, *Journal of Archaeological Science* 39, 2361-2370.

The Harea-Coastal Geology research group has a leading role in the Postgraduate Programmes (Master and Doctorate) and the UFI 11/09 on Quaternary: Environmental Changes and Human Footprint ([www.mastercuaternario.ehu.es](http://www.mastercuaternario.ehu.es)).

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# Global Boundary Stratotype Section and Points (GSSPs) in the Basque Coast

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KEY WORDS: Cretaceous, Palaeogene, Stratotype, Stratigraphy, Micropalaeontology.

The geological Time Scale is a valid global frame divided into intervals (Eons, Eras, Periods, Epochs and Stages) whose definition is based primarily on Stratigraphy, i.e., the study and interpretation of strata or layers of rocks formed by the accumulation of sediments. The International Commission on Stratigraphy (ICS) is responsible for selecting the geological sections worldwide that best represent the boundaries between unit intervals, i.e., the stages. Stage boundaries are defined by Global Stratotype Sections and Points (GSSPs).

The “Cretaceous and Paleogene working Group” of the Faculty of Science and Technology has organized several international meetings in 2006, 2007 and 2009, which showed the International community, and ultimately the ICS, the high geological quality of the Basque coastal cliffs. These are a worldwide reference to observe and study sedimentary rocks accumulated in deep-marine settings during the geological time that extends from the Early Cretaceous to the Eocene, a lapse interspersed with some of the most significant global change events. As a result of these meetings, the Itzurun beach at Zumaia was selected as the stratotype section for the Danian/Selandian and Selandian/Thanetian boundaries and the Gorrondatxe Beach was selected for to define the stratotype for the base of the Lutetian stage.

## The GSSPs for the bases of the Selandian and Thanetian stages

The global stratotype sections and points for the bases of the Selandian (Middle Paleocene) and Thanetian (Upper Paleocene) stages have been defined in the coastal cliff along the Itzurun Beach at the town of Zumaia in the Basque Country, northern Spain. In the hemipelagic section exposed at Zumaia the base of the Selandian Stage has been placed at the base of the Itzurun Formation, ca. 49 m above the Cretaceous/Paleogene boundary. At the base of the Selandian, marls replace the succession of Danian red limestone and limestone-marl couplets. The best marine, global correlation criterion for the basal Selandian is the second radiation of the important calcareous nannofossil group, the fasciculiths. Species such as *Fasciculithus ulii*, *F. billii*, *F. janii*, *F. involutus*, *F. pileatus* and *F. tympaniformis* have their first appearance in the interval from a few decimetres below up to 1.1 m above the base of the Selandian. The marker species for nannofossil Zone NP5, *F. tympaniformis*, first occurs 1.1 m above the base. Excellent cyclostratigraphy and magnetostratigraphy in the section creates further correlation potential, with the base of the Selandian occurring 30 precession cycles (630 kyr) above the top of magnetochron C27n. Profound changes in sedimentology related to a major sea-level fall characterize the Danian-Selandian transition in sections along the margins of the North Atlantic. The base of the Thanetian Stage is placed in the same section ca. 78 m above the Cretaceous/Paleogene boundary. It is defined at a level 2.8 m or eight precession cycles above the base of the core of the distinct clay-rich interval associated with the Mid-Paleocene Biotic Event, and it corresponds to the base of magnetochron C26n in the section. The base of the Thanetian is not associated with any significant change in marine micro-fauna or flora. The calcareous nannofossil Zone NP6, marked by the first occurrence of *Heliolithus kleinpellii* starts ca. 6.5 m below the base of the Thanetian. The definitions of the global stratotype points for the bases of the Selandian and Thanetian stages are in good agreements with the definitions in the historical stratotype sections in Denmark and England, respectively.

## The GSSP for the base of the Lutetian Stage.

The GSSP for the base of the Lutetian Stage (early/ middle Eocene boundary) is defined at 167.85 metres in the Gorrondatxe sea-cliff section (NW of Bilbao city, Basque Country, northern Spain; 43°22'46.47" N, 3° 00' 51.61" W). This dark marly level coincides with the lowest occurrence of the calcareous nannofossil *Blackites inflatus* (CP12a/b boundary), is in the middle of polarity Chron C21r, and has been interpreted as the maximum flooding surface of a depositional sequence that may be global in extent. The GSSP age is approximately 800 kyr (39 precession cycles) younger than the beginning of polarity Chron C21r, or -47.8 Ma in the GTS04 time scale. The proposal was approved by the International Subcommittee on Paleogene Stratigraphy in February 2010, approved by the International Commission of Stratigraphy in January 2011, and ratified by the International Union of Geological Sciences in April 2011.

# Geological multidisciplinary research of Quaternary period

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KEY WORDS: Quaternary, fossil remains, archaeological materials.

This line of research is formed by a multi-disciplinary team and combines a set of interrelated projects on which a group of senior and junior members have been collaborating during the last few years. The researching team consists of palaeontologists, archaeologists, mineralogists, petrologists and geochemists.

Two main scientific areas are investigated:

1. **Palaeoclimatic and palaeoenvironmental reconstructions** in the southern Bay of Biscay in the last 100 or 120 thousand years. These reconstructions are able for comparison with other local, regional and global registers as pollen, GISP2, the marine record, etc.
2. **Human technological evolution** to provide clues of their technological skills and also cultural and trade links.

## PALAEOCLIMATIC AND PALAEOENVIRONMENTAL RECONSTRUCTION

Several types of fossil remains are considered as palaeoenvironmental proxies:

- **Marines invertebrates** i.e. Rodríguez-Lazaro J., Pascual A., Martínez García B. (2013) *Journal of Marine Systems* 109-110, S213-S232.
- **Terrestrial invertebrates** i.e. Murelaga X., Ortega L.A., Sancho C., Muñoz A., Osácar O., Larraz M. (2012) *The Holocene* 22, 1047-1060.
- **Small mammals** remains from caves i.e. Rofes J., Zuluaga M.C., Murelaga X., Fernández-Eraso J., Bailon S., Iriarte M.J., Ortega L.A., Alonso-Olazabal A. (2013) *Quaternary Research* 79, 158-167.
- **Large mammals** remains from caves i.e. Castaños J., Zuluaga M.C., Ortega L.A., Murelaga X., Alonso-Olazabal A., Rofes J., Castaños P. (2013) *Quaternary International*. doi: j.quaint.2013.10.006.
- **Human remains isotope analysis** can be used to establish mobility patterns. Ortega L.A., Guede I., Zuluaga M.C., Alonso-Olazabal A., Murelaga X., Niso J., Loza M., Quirós Castillo, J.A. (2013) *Quaternary International*, 303, 54-63.

## HUMAN TECHNOLOGICAL EVOLUTION

Archaeometric research are performed on several types of historical materials:

- **Megalithic tombs** i.e. Suarez-Hernando O., Baceta Caballero J.I., Murelaga Bereikua X. (2011) *Kobie Serie Paleoantropología*, 30, 73-82.
- **Ancient pottery** archaeometric studies i.e. Zuluaga, M.C., Alonso-Olazabal, A., Olivares, M. Ortega, L., Murelaga, X., Bienes, J.J., Sarmiento, A., Etxebarria, N. (2012) *Journal of Raman Spectroscopy*, 43, 1811-1816.
- **Historical lime mortar** research i.e. Ortega L.A.; Zuluaga M.C.; Alonso-Olazabal A.; Murelaga X.; Insausti M.; Ibañez-Etxebarria A. (2012) *Radicarbon*, 54, 23-36.

# Mass transfers through the lithosphere

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KEY WORDS: lithosphere, delamination, tectonics, structural geology, transpression, extensional collapse

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Our main research topics are the mass transfers in the continental crust, a key point for the dynamics of the lithosphere. The most important processes of mass transfer through the lithosphere are due to the motion of ductile shear zones and the intrusion of huge volumes of igneous rocks. They are mainly concerned with the links between the intrusion of plutonic rocks and the nucleation and development of ductile shear zones.

We integrate field studies of Structural Geology, rock fabric analyses, measurements of the anisotropy of the magnetic susceptibility and gravity data in order to perform 3-D models. Since this approach is concerned with geological processes rather than with regional questions, we have selected a few working areas which encompass the main steps of a complete orogenic cycle:

- **Oceanic subduction** in La Puna and the Eastern Cordillera (Salta, NW Argentina), with special emphasis on the Calama-Olacapato-El Toro lineament, representing a transfer zone associated to an important change in the subduction angle of the Nazca plate below the South America plate. Magmatism, recent volcanism and active seismicity related to mantle delamination of the South American plate can be also tested in this area.
- **Continental collision and transpression**, in the Central-Iberian Zone of the Iberian Variscan belt and in the central and western Pyrenees. In the Pyrenees the study analyses the evolution from continental collision to transpression during the Hercynian orogeny (Benasque and Panticosa sectors) and the superposition of the Alpine orogeny. In the Central-Iberian Zone we are mainly working in the internal structure and emplacement of granite plutons, as a way to test the influence of lithospheric delamination in old orogens.
- **Extensional collapse**, in Betic Cordilleras. The interest of this area is due to the presence of the Ronda peridotites, the largest outcrops of the subcontinental mantle in the world, which allows a unique chance to analyse the deformation of the lithospheric mantle at the Earth's surface.

All of these areas are suitable to test melt-enhanced deformation processes related to the interplay between shear zones and igneous melts. The members of the applying institutions, Universidad del País Vasco and Salamanca in Spain and CONICET in Argentina, have the methodological and regional expertise required for this type of works. The results of this research represent a significant advance in the knowledge of both, the emplacement of granite plutons and the rheological behaviour of rocks during the nucleation, kinematics and evolution of ductile shear zones. These are essential factors for the geodynamic interpretation of orogenic belts.

# Development of advanced materials for the generation, storage and liberation of energy

IMaCris/MaKrisl Research Team

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KEY WORDS: Energy generation and storage, advanced materials, SOFC cells, batteries, MOFs, sensors, catalysis.

The IMAcris/MaKrisl research group focuses its work on the fields of Materials Science, Crystallography and Solid State Chemistry, having as target the applicability of the developed materials. The current research is based on two complementary approaches: Approach 1: *EGS Materials (Energy Generation and Storage)* and Approach 2: *GSS Materials (Gas Sensor and Storage)*. In the first approach, the goal is to optimize materials for their use in primary and secondary batteries and solid oxide fuel cells (SOFC). Concurrently, Approach 2 is based on the rational design of flexible porous materials with potential adaptability to enclose, store and detect gases.



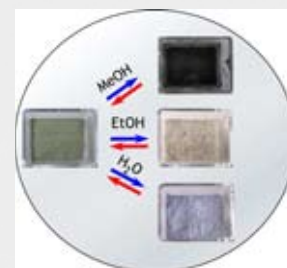
**Figure 1.** Interconnect/contact layer/cathode system.

Respect to the SOFCs, the research group, in collaboration with the Ecole Polytechnique Fédérale de Lausanne (EPFL), the Ikerlan Technological Research Center, the Materials Science Institute of Aragón (ICMA-CSIC) and the School of Chemistry at the University of Birmingham have studied the chemical reactivity and realized the optimization of different SOFC materials:  $AFeO_{3-\delta}$  ( $A = Ln_{0.5}M_{0.5}$ ) cathodes, barrier of SDC ( $(CeO_2)_{0.8}(SmO_{1.5})_{0.2}$ ) between the cathode and electrolyte, electrochemical durability of metallic materials used as interconnects and different  $ABO_3$  perovskite materials as cathode contact layers (See Figure 1).

With regard to inorganic cathodes for batteries, our research group is developing vanadium and silver nanostructured hydrogels, with potential applications as cathode material in primary batteries for implantable cardioverter defibrillators, and vanadium hybrid layered compounds as cathode materials for secondary  $Li^+$  and  $Na^+$  batteries. In addition, our group, in collaboration with ICMA-CSIC, the School of Chemistry at the University of Birmingham and the Pontifical Catholic University of Peru, has optimized the preparation and processing of  $Li_{3x}Ln_{2/3-x}TiO_3$  titanates, improving its electrochemical response as solid electrolytes.

Regarding the GSS materials outlined in Approach 2, our research group has extensive experience in the design of zeolite type porous materials with different compositions and structures (zeotypes). The research group IMAcris/MaKrisl, in collaboration with the Institute of Materials Science of Madrid (ICMM-CSIC), has carried out catalytic activity studies (cyanosilylation of aldehydes and selective oxidation of organic sulfides and alkenes) of different compounds. The last four years our research group has developed a second line of GSS materials based on metal organic frameworks or MOFs. Such materials exhibit a flexible response to heat treatments, enabling their activation for using them in various processes, such as, catalytic, sensing and/or storage of pollutants and/or hazardous molecules, chemical sensors, electroluminescent and electrochromic devices.

The continued progress of the research group has enabled a step forward in the chain of knowledge transfer to the society. In this regard, we have studied the reversibility and recyclability of a coordination polymer, which is capable of exchanging water molecules for other organic solvents such as methanol, ethanol and isopropanol (Figure 2) enabling the design of a sensor device of the mentioned alcohols, which can be used as a breathalyzer (patented invention). Recently, we have started to work on GSS materials based on porphyrins found in nature which are capable of mimic biological functions. Preliminary studies with metalloporphyrin compounds as catalysts have shown that are active for acetylation and oxidation of alcohols and amines.



**Figure 2.** Coordination polymer used as a chemical sensor of different alcohols.

## Acknowledgements Latest Publications/Patents of IMAcris/MaKrisl Research Team

MICINN: Ceram. Int., (2014) DOI 10.1016/j.ceramint.2014.01.097; J. Solid State Chem., (2014) DOI 10.1016/j.jssc.2014.01.013; Cryst. Growth Des., (2014) DOI 10.1021/cg401540s; J. Power Sources, 248 (2014), 1067-1076; Solid State Ionics, 235 (2013), 14-21; Fuel Cells, 13(3) (2013), 398-403; J. Power Sources, 243 (2013), 419-430; Dalton Trans., 42 (2013), 12481-12494; Dalton Trans., 42 (2013), 4500-4512; Inorg. Chem., 52 (2013), 2615-2626; Inorg. Chem., 52 (2013), 8074-8081; CrystEngComm., 15 (2013), 4181-4188; Patent: "Alcohol and water sensor compounds, detection method and device", PCT/ES2012/070723.

Matematika



Matemáticas

# Biostatistics Research Group

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KEY WORDS: Biostatistics; Clinical research; Transfer

The main specific objectives of the group are to detect problems of scientific interest in the biomedical and experimental fields where biostatistics can contribute to their resolution; conduct our own research in biostatistics aimed at generating results for solving the problems; create necessary computer tools and software for its implementation; and apply the proposed methods to the considered problems, helping to interpret the results and draw final conclusions, in collaboration with biomedical and experimental researchers involved.

Other objectives of the group are basically transversal, such as, to give methodological support in biostatistics to other research groups in the fields of biomedicine or experimental sciences; to promote the transfer of the research done at the university in biostatistics to biomedical and experimental fields; to take advantage of the strong demand for support in biostatistics to detect future research in this area, that respond to real problems in other fields.

## ACTUAL RESEARCH TOPICS:

1. **Development of prognostic severity scores for risk stratification.** Limited information is available about predictors of short-term outcomes in patients with chronic diseases. We propose a method for the development of prognostic severity scores for risk stratification and to make them available as easy to use tools for clinical decision-making process. The proposed methodology starts with the development and validation of prediction models that are converted to valid severity scores and categorized for risk stratification. Methods for internal and external model validation and methods for optimal categorization are properly combined into the whole process.
2. **Development of an overall score of evaluation from the responses to a questionnaire.** The first factorial axis of Multiple Correspondence Analysis defines a logical and ordered scale of the different modalities of responses. If we assign to each modality their first factorial coordinate and we obtain the arithmetic mean of the factorial coordinates of the chosen modalities, this average provides an overall measure of evaluation that, by linear transformation, we can turn into an evaluation score from 0 to 100.
3. **Categorization of continuous predictors.** In daily clinical practice researchers encourage statisticians to categorize continuous variables. Our proposal consists on categorizing a continuous predictor  $X$  in such a way that the best predictive logistic regression model is obtained in terms of the highest area under the receiver operating characteristic (ROC) curve (AUC). With this goal, we have developed two approaches named AddFor and Genetic, which have been compared and validated by means of simulations. This methodology has been applied to real clinical data with satisfactory and face-validated results.
4. **Development of predictive models of evolution for patients with chronic diseases: Implementation in technological tools.** Once developed clinical prediction models are implemented in an easy to use software tool. Clinicians can automatically obtain the model based results for each patient and use it as support in the decision-making process. A computer tool for different environments called PREVEPOC has been developed. By using this tool, clinicians can stratify patients with eCOPD attending the ED depending upon their risk of mortality or bad evolution in a short period of time.

FOR MORE INFORMATION LOOK AT THE FOLLOWING WEB PAGE

<https://sites.google.com/site/biostit/>

# Stochastic Optimization and Parallelization

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KEY WORDS: stochastic optimization, risk, stochastic dominance constraints, parallelization, CPLEX, COIN-OR.

Stochastic Optimization (SO) is broadly studied and applied in today's real-world applications. Uncertainty is the key ingredient in many decision problems. There are several ways in which uncertainty can be formalized and over the past thirty years different approaches to optimization under uncertainty have been developed. The field of SO appeared as a response to the need to incorporate uncertainty into mathematical optimization models.

Basically, it deals with situations in which some parameters are random variables (i.e., coefficients in the objective function, the right hand side vector and the constraint matrix). It allows the risk inherent into the random variables of the problem to be managed, or at least partially managed.

In the general formulation of a multistage stochastic integer optimization problem, decisions on each stage have to be made stage-wise. Moreover, there have been few attempts to solve large scale general multistage stochastic mixed 0-1 models up to optimality due to their complexity. In any case this type of problems require an intensive computing effort, even using decomposition algorithms for problem solving. Parallel Computing (PC) offers an alternative for solving very large scale problems by parallelizing the solution of mixed integer submodels that appear in the decomposition algorithms and parallelizing the execution of some steps of the algorithms. We have implemented the parallel version of the Branch and Fix Coordination Multistage algorithm (P-BFC). The parallelization is performed at two levels, inner and outer. The elapsed time required by outer-inner parallelization is very frequently some orders of magnitude smaller than that of the sequential version of the algorithm, depending on the computer resources available.

The stochastic optimization models consider, in general, the optimization of the objective function expected value alone (so, the risk neutral (RN) environment is assumed). However, the optimization of the RN objective function has the inconvenience of providing a solution that ignores the variability of the objective function value over the scenarios. There are some approaches that additionally deal with risk measures in the more realistic risk aversion environment. These measures consider semi-deviations, excess probabilities, conditional value-at-risk and stochastic dominance as risk measure-based functions to optimize. Recently, new risk averse measures for two-stage stochastic mixed 0-1 problems have appeared in the literature, in particular, the so named first- and second-order Stochastic Dominance Constraint (SDC) recourse-integer strategies for a set of profiles included by pairs of thresholds on given function values and some types of shortfall related bounds on reaching them. We are studying the multistage time consistent mixture of those two SDC measures. The SDC measure that we propose is included by user-driven set of profiles, each one consists of a threshold on the value of a function, a  $\beta$ -bound target for the shortfall probability and an  $e$ -bound target for the expected shortfall of the scenario to occur as soft constraints whose violations are appropriately penalized in the objective function, and a hard bound on the maximum shortfall. In order to keep time consistency the thresholds are intended over the scenario objective function up to a set of user-chosen stages along the given time horizon. Those approaches are more amenable than the classical mean-variance schemes. We study the risk aversion strategies in the applications using the decomposition algorithm so-named BFC-SDC.

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# Matrix analysis and applications group

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KEY WORDS: matrix analysis, control theory, linear systems, structure invariants, perturbation, numerical linear algebra, inverse problems, canonical forms, eigenvalues, singular values.

The Group of Matrix Analysis and Applications (GAMA) of the University of the Basque Country is the result of the evolution of a team that has been working uninterrupted in research since 1981. The main research areas of this group are:

- Theory of matrices.
- Mathematical control theory.
- Perturbation theory.
- Numerical linear algebra.

The aim of our research is to gain insight into the structure of the linear control systems and matrices and to develop mathematical techniques in order to solve problems in these areas. The following research lines have been designed:

- Study of the structure of control systems and matrices.
- Spectral perturbation of matrices and linear systems.

These research lines are closely related. Nevertheless, in order to clarify the problems that we are interested in, we will state, in a general manner, some of them:

1. Pole assignment to singular systems by state feedback and output injection.
2. Study the geometry of solutions of the cover problem with stability.
3. Study the topology of the generalized partial realization problem.
4. Study the relationship between the Wiener-Hopf factorization indices and the indices given by biproper rational matrices with prescribed finite structure.
5. Obtain reduced forms for the equations that define a bimodal piecewise-linear system and characterize structural properties such as controllability and stability for this type of system.
6. Extend the concept of controlled invariant subspace to bimodal piecewise-linear systems, studying its geometry and its potential applications.
7. Study the change of the controllability indices of a controllable pair when the elements of a column of the control matrix are slightly perturbed.
8. Find the distance from a given matrix to the set of matrices with less generic prescribed Segre's characteristic and characterize the multiple pseudospectra of normal matrices.

The methods and techniques to be used run over almost all fields of mathematics: from Linear Algebra and Matrix Analysis or Combinatorics to Differential Geometry or Commutative Algebra.

Weekly seminars are kept where the progression of the subgroup's work is shown, the difficulties are discussed and other researchers' work related to our problems is explained. This and the individual study of papers are the main methodological tools. The results are published in the most important specialised journals: Linear Algebra and its Applications, SIAM Journal of Control and Optimization, SIAM Journal on Matrix Analysis and Applications, International Journal of Control, Linear and Multilinear Algebra, Electronic Journal of Linear Algebra, etc.

More information in: <http://www.ehu.es/gama>

# Optimising the manufacture of offshore mooring chains in Vicinay Cadenas

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KEY WORDS: Flash Butt Welding, Mooring Chains, Optimization.

Vicinay Cadenas S.A. (VCSA) is a steel processing company that specialises in the manufacture of chains and accessories for mooring lines used in the offshore industry, mainly for oil and gas. Its main customers are major oil companies such as Exxon, Shell and BP, which require mooring systems for their offshore rigs. VCSA makes chains of various types to order for its customers, and is a world leader in its field.

Welding is a key part of chain manufacturing. This study seeks to determine how the manufacturing parameters of welding machines influence the appearance of inhomogeneities. The idea is to optimise current manufacturing processes and acquire knowledge that will enable the firm to develop new products with diameters in excess of those produced to date. To that end, multivariate analysis techniques are used to study manufacturing data on various chains and an algorithm is designed that selects the spreads of the adjustable variables that contain the lowest (highest) percentage of links with inhomogeneities.

	Full range	Best spreads
Variable $x_1$	773.14 - 878.32	804.800 - 852.210
Variable $x_2$	163.303 - 172.157	166.920 - 172.050
Variable $x_3$	40.045 - 43.14	40.81 - 42.75
Variable $x_4$	15.162 - 20.558	15.65 - 18.03
Variable $x_5$	44.798 - 47.95	44.800 - 47.040
Variable $x_6$	0.807 - 0.944	0.862 - 0.944
Variable $x_7$	172.578 - 186.032	178.82 - 186.030
N° of links	8.855	1.000

Manufacturing run "B". Full range of the adjustable variables and spreads of those variables containing 1000 links and the lowest concentration of inhomogeneities

The method designed for locating the best and worst spreads of the welding variables was then applied to nine manufacturing runs of chains with different diameters on the same machine, with a view to drawing up a table of settings for it. The results show that the nominal figures for the variables increase when the diameter of the links to be welded increases, in a way that is consistent with the experience of the company. This has led to a modification of the whole table of settings for the machine. The new table is an improvement on the one currently in use at Vicinay Cadenas S.A. The results also provide an estimate for the table or settings that needs to be applied to tackle the manufacture of new, larger chains.

# Topological and non-commutative techniques in the study of foliated spaces

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KEY WORDS: foliated space, lamination, Riemannian foliation, noncommutative geometry

Our research consists of the dynamic and cohomological study of foliated spaces, and the analytic and K-theoretical study of the corresponding noncommutative spaces.

Nowadays, foliation theory is a multidisciplinary field, essentially non distinguishable from dynamical systems theory. It involves several and complex geometric, topologic, analytic and measurable techniques. In the last decades, the specialists in the subject have developed new fruitful research lines by removing some of the restrictions imposed to classical foliated manifolds. In particular, our group focuses its work in:

- 1) the study of some types of singular foliations (removing the regularity conditions);
- 2) the study of foliations induced by the orbits of the action of a Lie group on a manifold;
- 3) The study of algebraic invariants who describe the transverse structure of foliations;
- 4) the noncommutative study (à la Connes) of some foliated spaces (deletion of commutativity).

Foliation theory is playing and will play a fundamental role in the qualitative study of both the physical (cosmology and solid state physics) and the biological world (molecular biology, genomics and evolution), and appears increasingly in other science fields.

Our concrete objectives can be classified in two main blocks:

- 1) The study of metric and dynamical properties of foliated spaces and its relations. Tilings and repetitive graphs give us examples of minimal laminations, useful in the testing of properties and relations. Moreover, noncommutative geometry gives topological and measurable tools that allow us to complete this study (see [1], [2]).
- 2) Cohomological study of Riemannian foliations. We study the relation between the basic cohomology and the cohomology of the ambient manifold, through algebraic tools such as exact sequences and spectral sequences, for both regular and singular Riemannian foliations (see [3], [4] and [5]).

Last publications:

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# GRECA: Groups, Representations and Combinatorial Algebra

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KEY WORDS: Finite p-groups, pro-p groups, characters, representations, algebraic combinatorics.

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The research of this group is organised around four main areas, which we describe below:

## 1. Finite p-groups

In this area, we focus on the following two topics: the power structure, and the conjugacy classes, both of elements and subgroups. In the first case, our goal is to obtain families of p-groups which, as far as taking powers is concerned, resemble abelian groups (for which the identity  $(xy)^n = x^n y^n$  holds for every exponent n). In the case of conjugacy classes, we investigate what properties can be deduced about a finite p-group if we fix the number of classes.

## 2. Pro-p groups

Currently, pro-p groups is one of the most trendy research topics in group theory. These groups provide a way of studying simultaneously a family of finite p-groups whose order grows to infinity. In this field, we are working on several problems: power structure, (co)homology, and word problems such as the width of a word and the effect of a positive law on the values of a word. In the case of the word problems, we focus on p-adic analytic groups.

## 3. Characters

We work on several problems related to characters and representations, mainly on finite p-groups. Even if the representations of classical groups over finite fields are well understood, there is not a satisfactory theory of the representations of their Sylow p-subgroups, and we are interested in this problem. In another direction, we are analysing how the degrees of the irreducible representations or the values taken by the characters have an influence on the structure of a finite group.

## 4. Algebraic Combinatorics

We look for t-designs, and more specifically 2-designs, that have nice symmetry properties, in the sense that they admit a group of automorphisms that acts regularly on its points. We are also working on the construction of combinatorial structures linked to differences in finite groups, such as difference sets, difference families, and cyclic association schemes.

Kimika



Química

# Natural products in foods, beverages and plants

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KEY WORDS: Polyphenols, anthocyanins, red wine, fruits, medicinal plants, vegetables, microalgae, cyanobacteria, nutraceuticals, antioxidant, encapsulation.

Determination of the chemical composition of foods and beverages has a huge interest from many points of view. A deep knowledge of natural products in foods can lead to improve nutritional quality or to detect geographical origins, manufacturing methods, bad practices, adulterations and frauds.

Polyphenols are a very important group of natural products due to their ubiquity in the vegetable kingdom, and their interest as a key to explain many food properties such as flavor, astringency, aroma and color, besides their known beneficial effects on human health (e.g. lower risk of heart diseases and cancer).

With this aim and after successful works in ciders, apples and edible oils, our research group is currently working in the following projects:

- Anthocyanin analysis in red txakolis of Biscay and in extracts of freeze-dried grape pomace for the evaluation and control of vinification procedures, and of quality parameters related to the local Protected Designation of Origin, such as wine color; which is one of the most important parameters directly related to anthocyanins.
- Volatile compounds analysis in txakoli by *fast* gas chromatography: Volatiles are responsible for wine aroma, which is a feature that gives information to the wineries about the course of vinification, critical process for the final quality of wine.
- Characterization of the polyphenolic profiles of agricultural food products (fruits, vegetables, fruit derived foods, cider, wine) determined by HPLC-DAD and HPLC-MS/MS: Polyphenolic composition provides a tool for quality control, as well as for authentication, and detect adulterations and bad practices in food manufacturing by using chemometrics (PCA, MLR, PLS, LDA, PLS-DA, neural networks), among others.
- Study of anthocyanic derived pigments in aged red wine from “*Rioja Alavesa*” formed in specific reactions during barreling. These pigments are determined by HPLC-DAD-MS/MS after sample clean-up by Solid Phase Extraction (SPE).
- Study of tannins in aged red wines from “*Rioja*”, which define to great extent wine properties, such as astringency and wine texture. Tannins are determined by SPE-HPLC-DAD-MS/MS.
- Use of the by-product generated in the agricultural food industry during manufacturing processes (apple pomace, grape pomace), obtaining high value-added bioactive molecules for the food, pharmaceutical and cosmetic industries.
- Study of the polyphenolic profiles of apples and apple juices, determined by UHPLC-DAD and UHPLC-QToF-MSE, in order to compare progenies of different apple genitors to implement new apple varieties in the market.
- Natural products in plants, microalgae and cyanobacteria in the search of high value-added bioactive

# FARMARTEM

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KEY WORDS: drugs analysis, metabolomics, pesticides, microencapsulation, fluorinated compounds, documents

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FARMARTEM is an analytical chemistry research group involved into different fields: determination of drugs and metabolomic studies, environmental and industrial analysis, and forensic studies of documents.

**DETERMINATION OF DRUGS AND METABOLOMICS** The drug analysis in biological fluids is the more consolidated research line of this group. Determination of drugs used in combined cardiovascular therapy, opioids in biological fluids (plasma, urine, saliva) and amphetamines in hair have been carried out using selective and sensitive analytical techniques: high performance liquid chromatography-mass spectrometry (HPLC-MS), ultra high performance liquid chromatography-mass spectrometry (UHPLC-MS) and gas chromatography-mass spectrometry. Different sample treatments (protein precipitation, solid phase extraction, pipette-tip extraction and solid phase microextraction) have been used due to the complexity of matrixes, low concentrations of analytes and reduced volume of sample. It is worthwhile to mention the introduction of dried blood spot (DBS) procedure as a new methodology in sampling. As an example of collaborative work carried in this line, a rapid, sensitive and reproducible LC-MS/MS method has been developed and validated for the determination of the synthetic opioid fentanyl in plasma and cerebrospinal fluid from a pharmacokinetic/pharmacodynamic study in newborn piglets. Inside the metabolomic studies line, targeted and untargeted metabolomics have been applied to clinical and toxicological fields. In this sense, research has been focused to optimization of plasma samples treatment for metabolomic profiles, search of biomarkers in hepatotoxicity studies, organ maturation studies in paediatric population, the study of the metabolic pathways altered by schizophrenia disease and study of changes in lipid profiles related to food challenges. The analytical platform utilized for metabolomics studies has been liquid chromatography coupled with mass spectrometry.

**ENVIRONMENTAL AND INDUSTRIAL ANALYSIS** In this research line, different multidisciplinary projects have been carried out. Analytical methods for the quantification of pesticides in several environmental matrixes have been developed and applied to water analysis and soils bioremediation studies. Other innovative area in which the group is involved is the microencapsulation of biocides. The microencapsulation technology has demonstrated several advantages from an environmental point of view. On the other hand, the use of natural products obtained from plants in the production of a specific and with great efficacy biocide for plagues control is other objective of this environmental research line in collaboration with chemical companies.

Regarding industrial analysis, ion chromatography and capillary electrophoresis are techniques used to develop analytical methods for quality control analysis of cationic and anionic impurities contained in inorganic fluorinated compounds. This quality control solves a vast problem found in fluorine industry and demonstrates the social and economical benefit of technological transference of knowledge.

**FORENSIC STUDIES OF DOCUMENTS** In this research line, two different topics can be distinguished: - Optic analysis of inks: which allows the detection of documental manipulations and the identification of writing tools (ballpoint pens, felt-tip pens, markers...). - Characterization and dating of inks: It is possible to determine the age of a document by analyzing the hand-written inputs. The analysis of the volatile components present in inks gives a correlation between their concentration and the age of the document. This can be done by liquid chromatography-mass spectrometry and/or gas chromatography-mass spectrometry. The analysis of other physical properties, such as the refractive index of the inks as they age, might open new perspectives for the non destructive dating of documents.

# Towards an Integrative Assessment on Global Issues in Environmental Chemistry and Cultural Heritage

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KEY WORDS: Development of applied analytical methods; Environmental chemistry; Material analysis

We live together with the surrounding chemicals -especially pollutants- without grasping very well their fate and behaviour in the environment, and essentially their effects on the living organisms and on materials. In the first case, we deal with the fate and behaviour of contaminants in the environment and, in particular, with the risks associated with the presence of those contaminants for the environmental and the human health. In the second case, we mean the effects on the building materials, artworks or archaeological materials. Most of those global issues require a multidisciplinary and an integrative approach to understand the processes that take part in the hazardous effects or in the degradation or restoration processes.

In environmental chemistry, the most active lines deal with the development of new sampling and analysis methods of micro-contaminants. Their main aims are to study the mechanisms of transport and transfer among the different natural compartments and to support the environmental risk assessment studies. In this sense, we are currently working on (i) the development of analytical methods for emerging pollutants (personal care products and pharmaceuticals) through chromatographic techniques (GC-MS, LC-MS-MS), (ii) the use of passive sampling devices to provide integrative levels of the presence of many contaminants in aquatic and atmospheric media, (iii) on the plant bioavailability processes of some emerging pollutants that can be amended through contaminated sewage sludge that is used as fertilizers and the effect of that bioavailability on human consumption, and finally, (iv) we are also studying the environmental impact of abandoned mines and quarries as well as the assessment of the environmental risks of the reuse of black slags.

In the cultural heritage field, one of the consolidated lines deals with the development of methods and strategies based on the use of non-destructive, non-invasive and hand-held portable equipments, especially when artworks are very valuable objects or they cannot be damaged nor sampled. Techniques such as Raman and infrared (FTIR) spectroscopies, X-ray fluorescence (XRF) or laser induced breakdown spectroscopy (LIBS) are of common use for those purposes. In addition to this, we also use microscopic techniques such as scanning electron microscopy (SEM) or atomic force microscopy (AFM) coupled to elemental and molecular analysis not only to characterise the original components of the objects, but also to determine the degradation products that are formed due to the impact of chemical contaminants or aggressive environmental conditions.

Finally, owing to the use of a wide range of analytical instrumentation and methodologies we have consolidated grounds in other fields such as the food analysis and processes (aroma analysis and functional foods), the application of nanoparticle induced surface enhance Raman spectroscopy (SERS) on tissue imaging (FT-IR and Raman images), or sea/estuarine water acidification processes (accumulation of CO<sub>2</sub>).

IBeA (*Ikerketa eta Berrikuntza Analitikoa*) is a consolidated group with 14 permanent staff members and more than 6 postdocs and 15 PhD students. IBeA leads several research topics in both the environmental chemistry and the cultural heritage and collaborates with many other groups of the UPV/EHU, and from other Spanish and European universities. Together with two other research groups of the UPV/EHU, we are active members of the Research Unit called *Global Change & Heritage*.



# Advanced spectroscopic techniques applied to solving chemical problems

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KEY WORDS: electronic spectroscopy, microwave spectroscopy, femtochemistry.

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A variety of high resolution and time-resolved spectroscopic techniques involving coherent radiation is presented, and their contribution to solving different problems of interest in chemistry and biochemistry is presented. Using electronic laser spectroscopy in supersonic jets, molecular systems of biological interest can be studied, such as stable molecules and intermolecular complexes bonded by non-covalent interactions. Rotational spectroscopy in the microwave region is a very high resolution technique that allows discriminating molecular structures in the gas phase, which are of interest in astrochemistry and biology, such as ribose. Femtosecond time-resolved laser spectroscopy allows to follow the ultrafast dynamics of the excited states of a variety of species, such as aromatic chromophores or prebiotic molecules, either in the gas phase or in solution. Finally, the combination of Fourier-transform infrared spectroscopy and microwave spectroscopy applies to the study of physico-chemical processes in atmospheric science, like hygroscopic and reactive properties of tropospheric aerosols and nucleation processes in secondary aerosols.

# Manufacturing of nanostructured materials and their biological applications

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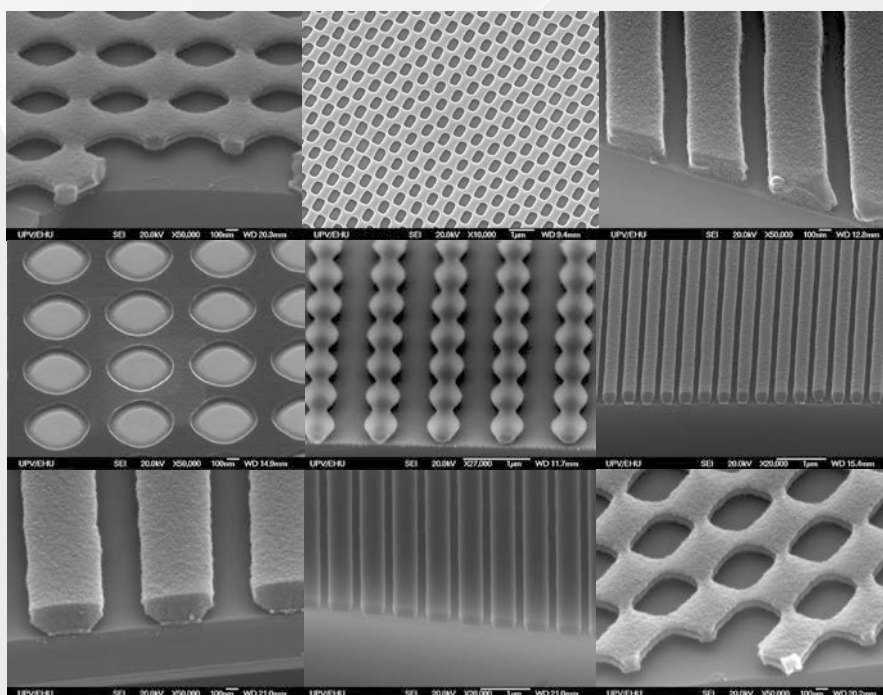
KEY WORDS: nanomagnet, nanotechnology, lipidomics.

The properties of nanostructures have been commenced to be exploited in applications related with a lot of functionalizations and nowadays their use in a variety of medical diagnostics and treatments is rapidly advancing. As an example, in the case of nanomagnets the new functionalizations are strongly favored due to their ability to act selectively in specific locations; moreover, the magnetic properties of these devices can be modified during the manufacturing process by controlling their design.

Due to the advances in nanotechnology, today it is possible to construct and manipulate nanoparticles having sizes comparable to many biological structures such as cells, genes, viruses or DNA chains. For that reason, these nanoparticles can interact individually with the biological entities and can selectively repair, eliminate or deliver medicines to cells.

The objectives of our research area in nanotechnology are the manufacturing and characterization of nanomagnets with biomedical applications, and also in a variety of electronic and data storage devices. In order to develop this research area we make use of several techniques, especially interference lithography (IL), due to its potential in combined processes of nanofabrication with IBS and lift-off techniques and to its versatility to control the nanomagnet geometry, size and thickness. Nanofabricated materials arranged in continuous films, multilayers and arrays are analyzed using the most advanced methods of nanocharacterization.

A different and relevant application of nanostructured materials is their possible use as active surfaces for the analysis of biological molecules by mass spectrometry. For example, in lipidomics, where the matrix can interfere with lipid detection, the use of active surfaces able to desorb the analyte is considered as an excellent alternative to the use of organic matrices. With this kind of devices it is possible to obtain the lipid distribution in tissue sections.



# Smart or Multifunctional Materials

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KEY WORDS: shape memory, piezoelectric, smart surfaces.

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Smart materials or multifunctional materials are **materials in which one or more** properties (shape, viscosity, colour,..) can be significantly changed in a controlled fashion by external stimuli, such as stress, temperature, moisture, pH, electric or magnetic fields.

Since smart materials first started to play an important role due to their capabilities to respond actively to environmental stimuli and enable significant potential applications, research on such materials has been progressively growing. The potential applications of such smart materials are abundant and include the design of smart aircraft skin embedded with fiber optic sensors to detect structural flaws, bridges with both sensor and actuating elements to counter violent vibrations, flying microelectromechanical systems (MEMS) with remote control for surveying and rescue missions and stealth submarine vehicles with swimming muscles made of special polymers.

Our laboratory is focused on the design and the synthesis of smart materials with susceptible properties to be useful as sensors and/or actuators. In this topic we are working in different research lines with the aim to develop new materials of different nature (organic, inorganic and hybrid) with specific properties as piezoelectricity or shape memory.

## RESEARCH LINES

- **Shape memory polymers.** Self-healing properties based on shape-memory features of covalently crosslinked semi-crystalline polyalkenamers were demonstrated by thermal-activated recovery of performed surface marks. The disappearance of surface defects was evaluated using non-contact confocal optical profilometry, as well as optical microscopy under heating processes. Alternatively, gamma radiation is employed to crosslink polycyclooctene chains to obtain shape memory polymers.
- **Smart polymer surfaces.** The profile or pattern surfaces and functionality determines the method and extent of the forces in a surface that interacts with its environment. So control of both the design and functionality of the surfaces allows to control these forces. The aim is to obtain surfaces capable of transforming environmental changes in a measurable signal. To generate the patterns we have relied on several techniques such as photolithographic and stamping techniques, among others. Molecules that have been used for this purpose are amphiphilic copolymers, namely a block copolymer of polystyrene (Ps) and polyacrylic acid (PAA).
- **Piezoelectric polymers.** The development of polymers with piezoelectric properties at high temperature is being studied. For this purpose, polyimides have been chosen due to their excellent thermal, mechanical and dielectric properties. Piezoelectric polyimides with polar groups (cyano groups, -CN) into the polymer backbone are synthesized. The polymer films are poled by two different methods: corona poling and contact poling. The magnetoelectric (ME) response of layered polyimide/epoxy/Vitrovac composites is also studied to use this composites for magnetic fields sensors in high temperature applications.

# A quantitative index for the electronic correlation degree in the N-electron wave functions.

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KEY WORDS: Reduced density matrices, Cumulant matrices, Electron correlation.

The effectively unpaired electron density matrix,  $u$ , was proposed as a tool to characterize the occupancy of different portions of space by spin-up and spin-down electrons<sup>1</sup>. Hence, it has been used as a measure of the radical and diradical character in molecules and transition states of any spin multiplicity<sup>2</sup>.

The cumulant of the second-order reduced density matrix provides a useful management of the correlated second order reduced density matrix in the description of properties of N-electron systems. The relationship between the spin-free version of the cumulant matrix and the unpaired electron density one was described some time ago<sup>3</sup>. It has been very useful in determinations of bond orders, valence and free valence indices in closed- and open-shell molecular systems<sup>4,5</sup>.

In this work we derive a simple relationship between the effectively unpaired electron density matrix, the well-known spin-density matrix  $P^5$  and the one-electron matrix arising from the diagonal contraction of the cumulant matrix  $\Gamma$  of the second-order reduced density matrix,  ${}^2D$ . This relationship allows one to decompose the number of effectively unpaired electrons  $N_u$  (the trace of the matrix  $u$ ), into two components<sup>6</sup>. One of them represents the number of net unpaired electrons arising from the spin. The second one accounts for the partial split of electron pairs that appears when correlated wave functions are used<sup>7</sup>.

This framework allows us to propose a quantitative index of the electronic correlation degree contained in the N-electron wave function<sup>8,9</sup>. Numerical determinations performed in selected systems with different spin symmetries confirm the theoretical predictions.

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# Photoactive Hybrid Materials

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*Iñigo López Arbeloa, Jorge Bañuelos, Teresa Arbeloa, Virginia Martínez-Martínez, Hegoi Manzano, Leire Gartzia, Ixone Esnal, Nerea Epelde, Rebeca Sola and Eduardo Duque.*  
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KEY WORDS: Laser Dyes, Zeolite, AlPOs, Metal Organic Framework, Atomistic Simulation, Photosensitizers, Nanoparticles, Photodynamic Therapy

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The encapsulation of photoactive molecules in different hosts results in composite materials with interesting promising applications in many technological and biomedical fields. The solid framework offers a rigid and robust environment for fluorescent molecules improving their emission capacity and thermal stability and infers a high organization degree. In this sense, the photophysical characterization of the dyes and dye-doped materials is a key factor to understand the involved processes or to develop new dyes with tailor-made physicochemical properties. Accordingly, quantum mechanical simulations have become a powerful tool to complement the experimental work and orient future strategies.

The Molecular Spectroscopy Group has accumulated a vast experience in the photophysical characterization of fluorophores (coumarines, rhodamines, BODIPY, pyronine, styryls, oxazines) with emission ranging from ultraviolet to the red part of the visible. To perform such study the laboratory is equipped with spectroscopic (absorption, and steady-state and time-correlated fluorescence) techniques and different fluorescence microscopies. These dyes have been characterized not only in solution but also in polymers, clays, zeolites and aluminophosphates as dopants. The obtained materials are being successfully applied in dye lasers, sensors, white light emitters and antenna devices, as result as of the consolidated collaborations established by the group in the last years.

Among the different research tasks of the group, five main research lines should be highlighted:

1. **BODIPY dyes.** Their photophysical properties can be controlled by the substitution pattern. Our interest in this field is focused on the spanning of their fluorescence and lasing region to the blue as well as to the red part of the visible. Furthermore, their chemical stability allows their use as sensors to monitor the environment characteristics or detect the presence of an analyte.
2. **Dyes doped 1D-nanostructures.** The encapsulation of guest fluorophores into the unidimensional pores of zeolite L and AlPOs leads to photoactive materials with interesting properties for applications such as antenna and white-light emitting devices, non-linear optics, colour switching, etc.
3. **Metal-organic frameworks (MOFs).** The design of a PCP with photoactive entities as part of the structure or confined in the pore as guests can contribute to the development of multiple applications such as molecular sensors, materials for laser, NLO properties, etc.
4. **Dyes doped nanoparticles.** By encapsulating two dyes (Rhodamine 6G and Nile Blue) with appropriate spectral overlap to give rise to an Energy Transfer process (FRET) into latex nanoparticles, a highly efficient and stable emission in the red region of the visible has been reached with applications for lasers in biomedicine. Furthermore, by the incorporation of photosensitizers into silica nanoparticles (embedded in or covalently anchored on the outer surface) a hybrid system with potential application in photodynamic therapy of cancer is desired.
5. **Atomistic simulation.** The above described systems are also studied by atomic scale simulations. We aim to complement experimental observations and help to understand the effect of confinement on the guest molecule's photophysics.

# QUANTUM TECHNOLOGIES FOR INFORMATION SCIENCE (QUTIS)

Íñigo Arrazola<sup>1</sup>, Hodei Eneriz<sup>1</sup>, Paul Pfeiffer<sup>1</sup>, Antonio Mezzacapo<sup>1</sup>, Urtzi las Heras<sup>1</sup>, Unai Alvarez-Rodriguez<sup>1</sup>, Roberto Di Candia<sup>1</sup>, Simone Felicetti<sup>1</sup>, Laura García-Álvarez<sup>1</sup>, Julen S. Pedernales<sup>1</sup>, Mikel Sanz<sup>1</sup>, Jorge Casanova<sup>1</sup>, Guillermo Romero<sup>1</sup>, Lucas Lamata<sup>1</sup>, Íñigo Egusquiza<sup>1</sup> and Enrique Solano<sup>1,2</sup>

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KEY WORDS: quantum physics, quantum information, quantum optics.

The research group "Quantum Technologies for Information Science (QUTIS)", based at University of the Basque Country in Bilbao, develops interdisciplinary research in Quantum Optics, Quantum Information, Superconducting Qubits, Circuit Quantum Electrodynamics, Condensed Matter, and Quantum Biomimetics. QUTIS is interested in theoretical quantum science with a deep comprehension of the involved quantum technologies. In this sense, we are constantly collaborating with experimental groups to confirm our predictions and models, and with an eye open for possible technological and patent applications.

1. **Quantum optics** is the study of the quantum properties of light and its interaction with quantum matter. It involves the description of atoms and molecules coupled with photons, laser and cavity fields. Quantum optics has produced a revolution in the fundamentals of quantum physics and has also contributed to numerous technological applications. It is expected that, along the 21st century, quantum optics can provide suitable quantum platforms for the implementation of quantum information protocols, including quantum computing and quantum simulations.
2. **Quantum Information** studies the merge of quantum physics and the classical theory of information, two key developments in the history of knowledge in the 20th century. It can be split into the following subfields: quantum computation, quantum simulation, and quantum communication. Quantum information has produced important milestones in our understanding of fundamentals of physics, as the concepts of entanglement, decoherence, quantum teleportation, quantum simulations, quantum computing, among many other fascinating topics. At the same time, it is expected that quantum information advances pave the way for future and emergent quantum technologies.
3. **Superconducting Qubits** are considered as artificial atoms made out of superconducting linear and nonlinear devices, and having as their main purpose the build-up of quantum computers and quantum information protocols with quantum circuits. **Circuit QED** represents the arrival of quantum optics to the microwave domain, via the implementation of coplanar waveguide cavities and transmission lines working at the quantum level due to the use of low cryogenic temperatures. The combination of superconducting qubits and circuit QED has produced an incredible boost in the development of quantum technologies with microwaves and superconducting mesoscopic systems.
4. **Condensed Matter** physics studies the condensed phases of matter, where the most common examples are liquids and solids. More elaborated examples include superconducting phases in some materials at low temperatures, ferromagnetic and antiferromagnetic phases of spins in atomic lattices, Bose-Einstein condensates, among others. Condensed-matter physics is arguably the largest field in contemporary physics, and it has merged recently with quantum optics for the sake of fundamentals, applications, and the implementation of quantum information ideas.

QUTIS has as a goal the development of top-level and influential interdisciplinary research with an international team of talented and motivated researchers. We aim at providing the best facilities, integration to national and international scientific networks, while keeping a friendly and competitive academic and research environment. Our PhD students and Postdoctoral Fellows are constantly driven by a research team spirit that stimulates their career growth with creativity, efficiency, good humor, healthy ambition, challenging thinking, and hard work. We try to promote a scientific philosophy where seniority and intellectual hierarchy means horizontal exchange of ideas with respect and motivation.

# New approaches for the development of porous materials based on metal-biomolecule frameworks (MBioFs)

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KEY WORDS: Porous materials, Coordination polymers, Metal-organic frameworks (MOFs), Metal-biorganic frameworks (MBioFs), Supramolecular Metal-biorganic frameworks (*supra*MBioFs) catalysis, gas adsorption and separation.

Metal-organic frameworks (MOFs) are a class of hybrid materials comprising metal ion-based vertices and organic ligands (linkers) that serve to connect the vertices into two or three-dimensional periodic structures. The structures and properties of MOFs can be carefully tailored by judicious selection of metal ion and organic linker building blocks.

A hallmark property of MOFs is their intrinsic porosity, which renders them potentially useful for gas storage, separations, catalysis, and a variety of additional applications that rely on highly specific host-guest interactions. Their promising properties coupled with the ease by which their structures can be modified make MOFs one of the most exciting, diverse, and rapidly growing areas of modern chemistry research.

Many potential applications of MOFs may require them to be constructed from benign building blocks that are biologically and environmentally compatible. For example, most biological applications, including drug delivery or intracellular imaging, would clearly require non-toxic MOF materials. In addition, many proposed applications will require bulk quantities of MOFs. To reduce their environmental impact, bulk MOF materials should be either environmentally compatible or easily recyclable. New generations of MOFs should be designed according to specific composition criteria that address their environmental and biological compatibility.

Recently, biomolecules have emerged as building blocks for constructing Metal-Biomolecule Frameworks (MBioFs). MBioFs are defined as MOFs constructed from at least one biomolecule which serves as an organic linker. Biomolecules offer several advantages as building blocks, which are highlighted here:

- Simple biomolecules, including amino acids, nucleobases, sugars, and others, are readily and naturally available in quantities and at prices amenable to preparing bulk quantities of materials.
- Biomolecules can lead to biologically-compatible MOFs.
- Biomolecules are structurally diverse. They can be either structurally rigid or flexible, aspects that impact the functional nature of the resulting MBioF.
- Biomolecules can have many different metal-binding sites. Consequently, they can exhibit multiple possible coordination modes, a feature that increases the potential structural diversity of MBioFs.
- Many biomolecules have intrinsic self-assembly properties which can be used to direct the structure and function of MBioFs.
- The ability of some of these biomolecules, specially in the case of nucleobases, to establish strong complementary hydrogen bonding favors the formation of open structures based on supramolecular non-covalent interactions (*supra*MBioFs).
- Finally, many biomolecules are chiral. Therefore, they can be used to construct chiral MBioFs, which may have interesting recognition, separation, and catalytic properties.

This suite of characteristics renders biomolecules particularly attractive building blocks for constructing MOFs with new properties and applications that cannot be accessed using the simple organic linkers traditionally used in MOFs construction.

# Nanostructured Materials of Technological and Biomedical Interest

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KEY WORDS: Li-ion and Na ion batteries, electrochemistry, spinel, sodium vanadium fluorophosphates, nanoparticles, thermal decomposition, superparamagnetism, electron magnetic resonance, magnetic hyperthermia

The work developed in this research group can be divided in two main lines: functionalized magnetic nanoparticles for biomedical applications and materials for energy. The first one explores magnetic nanoparticles for their application in different research fields such as biomedicine. The size confinement to nanometer scale in magnetic materials changes the properties from those of the bulk ferro and ferrimagnetic counterparts. These properties are interesting for some biomedical applications, such as drug delivery, MRI contrast or magnetic hyperthermia. In magnetic hyperthermia, an emerging alternative for the treatment of cancer, the size of nanoparticles, their stabilization and biocompatibility are key attributes that must be controlled. In this sense, nanoparticles must be in biological environment, requiring a proper optimization of the synthesis method and an adequate surface functionalization, which allows a good stability.

The most usual materials for such applications are the superparamagnetic iron oxide (SPIO) compounds, which have inverse spinel structure. Specifically, our work is focused on Fe<sub>3</sub>O<sub>4</sub> nanoparticles and nickel ferrites with different nickel composition to study the changes in magnetic properties. The nickel percentage range rises from 3 to 20 percent.

The second aspect covered by the group is the search for commercially viable Li-ion and Na-ion batteries, that is, more economic, safer and longer-life batteries. A substantial segment of the battery materials community is moving toward developing electrode materials on the basis of abundance and availability of the relevant chemicals. Regarding to lithium ion batteries, lithium manganese oxide spinel is especially interesting for use in hybrid electric vehicles and electric vehicles due to its low cost and high safety. However, the main problem for application is the capacity fading caused by the instability of Mn(III). In order to improve that factor, we investigate the effect of substitution of a small quantity of Mn by p-block elements such as Ga<sup>3+</sup> or Si<sup>4+</sup>, Li(Mn,M)<sub>2</sub>O<sub>4</sub> (M = Ga<sup>3+</sup>, Si<sup>4+</sup>).

On the other hand, the low cost, high abundance and ease of acquisition of sodium minerals promote interest in sodium-based electrochemical systems, especially for stationary energy storage devices. However, significant challenges such as energy density and long term stability must be addressed. In Na<sub>3</sub>V<sub>2</sub>O<sub>2x</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3-2x</sub> sodium-vanadium fluorophosphates are good cathodic materials for Na-ion batteries due to their high reaction voltages (at 3.6 and 4.1 V vs. Na/Na<sup>+</sup>) and their good specific capacity values in sodium half-cells (theoretical specific capacity of about 130 mAh/g) which leads to high energy density compounds (ca. 500 Wh/kg). Metal-air batteries are also studied due to their high energy density compared to traditional energy storage systems. This feature makes them suitable candidates for their application in the electric vehicle market.

Characterization of the different materials comprises powder X-ray diffraction (XRD), magnetic susceptibility measurements, EPR (Electron Paramagnetic Resonance), Electron Magnetic Resonance Spectroscopy (EMR), thermogravimetric analysis, Dynamic Light Scattering (DLS), Scanning and Transmission Electron Microscopy (SEM/TEM). Hyperthermia measurements are performed for nanoparticles with the highest magnetization values. The electrochemical measurements are conducted using coin-cell and Swagelok-type cells versus a metallic lithium or sodium anode.



# Polyoxometalates (POMs): Inorganic Building Blocks for Smart Materials

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KEY WORDS: Polyoxometalates, Hybrid materials, Smart surfaces. SCSC transformations

Polyoxometalates (POMs) are a large family of anionic clusters composed of oxo-bridged early transition metals from groups 5 and 6. These species are well-known because of their remarkable electronic versatility and structural diversity, which endow them with applications in numerous key areas including catalysis, biomedicine or nanotechnology. Since POMs offer a wide variety of compositions and shapes, they have been regarded as important building blocks for the construction of hybrid organic-inorganic materials, which are subject of great interest due to the possibility of combining active inorganic and organic components in a single material to get unusual structures and/or properties. Thus, a plethora of hybrid compounds made of POMs have been described in recent years

Four research lines within the POM-based organic-inorganic hybrid materials field are currently being developed in our group:

## **SELF-ASSEMBLED POMs WITH 3d/4f METALS**

This line is focused in the synthesis and structural characterization of novel POM clusters with unprecedented structures from the self-assembly of different POM precursors with first-row transition metals and/or rare earths. We are particularly interested in POMs with exposed 3d or 4f metal centers displaying at least two available coordination sites because these POMs could be subject of direct organic functionalization.

## **LANTHANIDE-CONTAINING POMs**

This line comprises the synthesis and structural characterization of novel Lanthanide-containing POMs. These POM families lead to dynamic libraries of building-blocks with the ability to undergo cation-directed self-assembly processes for constructing new POM architectures. The large structural diversity ranges from small dimeric species to giant POM clusters showing more than 100 metal atoms. Giant POMs slowly self-assemble in diluted solutions into hollow, single-layered and stable vesicle-like superstructures so-called "Blackberry-type" structures.

## **SINGLE-CRYSTAL TO SINGLE-CRYSTAL (SCSC) TRANSFORMATIONS**

The aim in this line is to synthesize and characterize hybrid metalorganic frameworks from the combination of POMs and first-row transition metal complexes with different organic ligands. These complexes can act as linkers of POMs to construct multidimensional hybrid lattices showing accessible pores or channels, making them good candidates for gas storage or as sensors. Derivatization with Cu<sup>II</sup>-LN4 complexes appears to endow POMs with interesting thermal behavior. Several compounds undergo single-crystal to single-crystal transformations promoted by reversible dehydration processes.

## **SMART SURFACES**

We are also interested in endowing surfaces made of organic polymers with additional properties provided by POMs through covalent anchorage of the latter components to the former surfaces. For this purpose, we have selected polystyrene surfaces with terminal polyacrylic functionalities and POMs with exposed 4f metal centers, in such a way that anchorage is made via coordination of the highly oxophilic 4f centers to carboxylate groups.

# Organocatalysis: New Synthetic Methodologies towards Sustainable Chemistry.

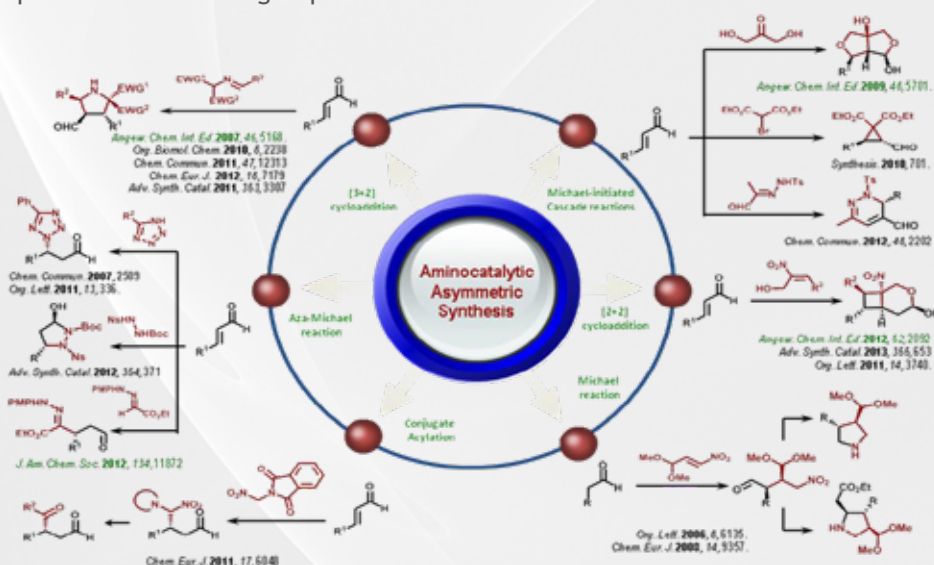
Jose Luis Vicario,\* Luisa Carrillo, Efraím Reyes, Uxue Uria, Garazi Talavera, Jose Ignacio Martínez, Iratxe Ugarriza, Ane Orue, Iker Riaño, Laura Villar, Liher Prieto, Eduardo Sánchez, Nagore Zabaleta, Raquel Mato, Asier Hidalgo, Alesandere Ortega  
Department of Organic Chemistry II, Faculty of Science and Technology, UPV/EHU.

KEY WORDS: Organocatalysis, Green Chemistry, Chiral Drug Synthesis, Asymmetric Catalysis.

Observing how Mother Nature solves complex problems in an easy way, the human being has been trying to imitate it for many centuries. Thus, the high catalytic efficiency of several enzymes in many natural processes has inspired many researchers to imitate and even improve its action, creating new protein-based biocatalysts. However, these show a rather narrow scope due to the inherent specificity of the biologic processes. For this reason, new and more flexible catalytic systems are needed for fine chemical production.

In asymmetric synthesis, not only should the catalyst accelerate the reaction but it also should be very stereoselective and flexible, in order to allow its use for the synthesis of different target molecules. In the last decade, organocatalysis has emerged as a very efficient tool in organic synthesis using small chiral organic molecules, which activate both reagents and reactants responsible for the stereocontrol of the reaction, in the absence of any metal. These organocatalysts are stable in air, water-compatible and easily prepared in both enantiomeric forms. Furthermore, most of them are commercially available, showing a great advantage when employed by pharma- and agrochemical industry, due to the fact that the presence of traces of contaminating transition metals is absolutely forbidden by legal regulations, avoiding additional purification methods.

Our research in this field has prompted us to study several organocatalytic methodologies and to the design of new catalysts which allow to carry out the reaction in water. These findings, together with the previously described advantages of organocatalysis compared to traditional metal catalytic reactions, are in accordance with the principles of Green Chemistry. Some of the following examples show the utility and the synthetic applications developed in our research group.



Our experience in Asymmetric Synthesis is well known and internationally recognized. Our research group provides laboratory facilities for students in the last year of degree, Master students, PhD. students or post-doctoral researchers. More information can be found in the group web page (<http://www.ehu.es/GSA>).

# Organometallics in Synthesis

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A. Gómez-SanJuan, E. Coya, E. Aranzamendi, I. Martín-Abraldes, V. Ortiz-de-Elguea, A. R. Azcargorta, I. Barbolla, I. Revuelta, A. Carral, M. Sánchez, S. Arrasate, H. González-Díaz, N. Sotomayor, E. Lete  
Departamento de Química Orgánica II, Facultad de Ciencia y Tecnología, Universidad del País Vasco /  
EuskalHerriko Unibertsitatea

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KEY WORDS: asymmetric synthesis, organometallics, chemoinformatics

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# New synthetic methodologies based on sustainable procedures.

Esther Domínguez, Raul SanMartin, Imanol Tellitu, Maria Teresa Herrero, Isabel Moreno, Maria Jesús Moure, Jokin Díaz de Sarralde, Garazi Urgoitia, Nerea Conde, Iratxe Astarloa, Yuliet A. Rincón, Izaskun Dávila<sup>1</sup>

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KEY WORDS: sustainable chemistry, metal catalysts, hypervalent iodine..

The two main research lines that are being conducted by our group are focused on the development of new synthetic methodologies to be carried out under sustainable conditions ("green chemistry").

## • NEW METAL CATALYSTS: DESIGN AND APPLICATIONS

We plan to design and synthesize new catalysts -mainly based on palladium, copper or iron- to be used in tiny amounts under sustainable conditions (aqueous or biodegradable media, possible reuse of the catalyst...). Our preliminary research shows excellent results for a variety of transformations as shown in Figure 1. The described optimized methodology has allowed us to prepare a number of polycyclic compounds of interest (see Figure 2) with the benefits of short synthetic sequences, economical advantages, and sustainability when compared to previous reported alternatives

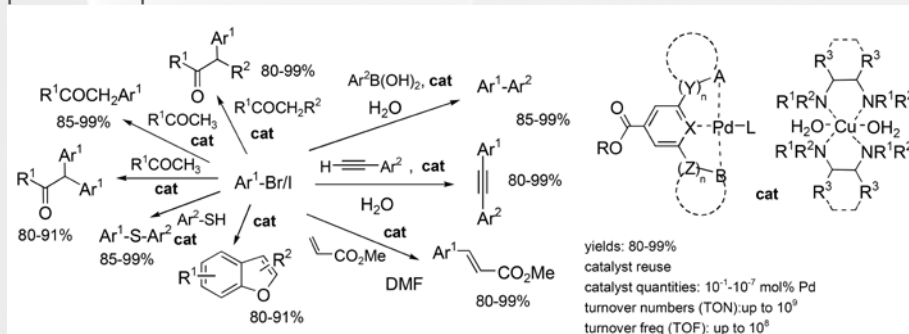


Figure 1. Selected reactions in which the new catalysts have been tested.

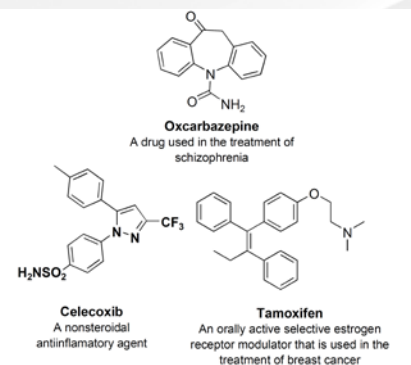
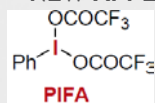


Figure 2. Target compounds prepared by the aid of the new catalysts.

## • NEW APPLICATIONS OF THE HYPERVALENT IODINE REAGENT PIFA



PIFA, [bis(trifluoroacetoxy)iodobenzene], has become a prominent reagent in our ongoing synthetic plans due to the soft reaction conditions that are required, its high efficiency, and its low toxicity.

One of the most attractive features of this reagent involves its ability to oxidize properly substituted amides to generate highly electrophilic nitrenium intermediates. If under such conditions our starting material contains an internal nucleophile, a cyclic compound can be formed.

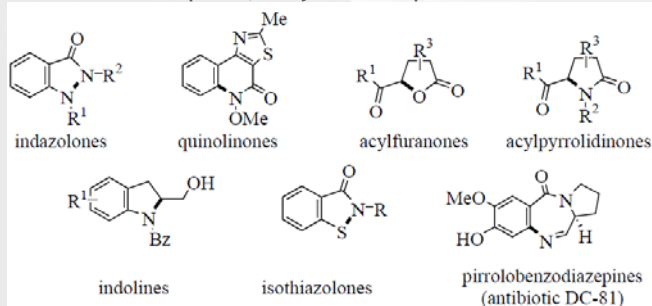
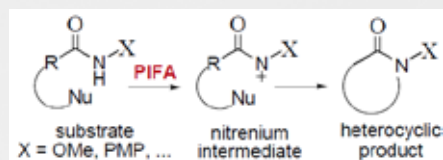


Figure 3. Selected examples of the use of PIFA in heterocyclic synthesis. The bond created by this reagent is highlighted.



The precise design of the substrates allows the preparation of a number of different heterocycles with high structural diversity (see Figure 3).

# Ingeniaritza kimikoa



# Ingeniería Química

# Processes for the sustainable production of fuels

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KEY WORDS: Bio-refinery, waste refinery, sustainable refinery, catalytic processes, catalysts, reactors

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In order to progress towards a Sustainable Refinery, biomass and consumer society wastes emerge as complementary sources to fossil ones (oil, coal, natural gas) for the production of fuels or raw materials, leading to two booming R&D&I platforms, namely, Bio-Refinery and Waste Refinery. The research group studies the technological development of key thermochemical and catalytic processes in these platforms (cracking, hydrocracking, reforming). The objective is the development of new processes at pilot plant scale, with continuous operation, in order to patent and/or make the technology demonstrable, bearing in mind their future industrial implementation integrated into the current refining processes.

## DESCRIPTION OF THE PROCESSES STUDIED

- Bio-refinery.** The contribution of the group to this platform focus on different processes with lignocellulosic biomass as raw material: a) bio-oil production by flash and catalytic pyrolysis of sawdust, agroforestry wastes, herbaceous biomass, sewage sludge; b) upgrading of the bio-oil and biomass derived oxygenates (methanol, ethanol, dimethyl ether) by means of acid catalysts into liquid fuels and raw materials (olefins or BTX); c) H<sub>2</sub> production by bio-oil and biomass derived oxygenate (ethanol, dimethyl ether) reforming; d) bio-oil cracking and hydrocracking under refinery conditions (FCC); e) direct synthesis of dimethyl ether.
- Waste Refinery.** This platform gathers the valorisation processes of consumer society wastes (plastics, tires) and secondary refinery streams: a) pyrolysis and steam gasification of different plastics (PE, PP, PET, PMM) and tires for the production of the corresponding monomers or fuels; b) two-stage pyrolysis-catalytic reforming and gasification-reforming of different wastes for H<sub>2</sub> production; c) methane upgrading into liquid fuels and olefins, (via chloromethane); d) catalytic cracking and hydrocracking of dissolved plastics and their derivatives (pyrolytic liquid) so as to obtain liquid fuels.

## TOOLS

The development of these processes involves the use and adaptation of Chemical Engineering tools, such as catalysts preparation and characterization, hydrodynamic studies, kinetic modelling, reactor design, process intensification, scale-up; accordingly, the improvement of each one of these tools is required.

## COOPERATION

The multidisciplinary nature of the work has promoted a solid cooperation with different Universities (Western Ontario, Saskatchewan, Calgary, Litoral, Delft, Utrech, Poitiers, Uberlandia, Espirito Santo, Amirkarbir, Chalmers, Roma, Leeds, Cantabria, Zaragoza), CSIC centers, companies of the power industry (Abengoa, Petronor) and research centers (Ikerlan IK4, Tekniker).

## FOR MORE INFORMATION

<http://www.ehu.es/cpwv>

# Innovations in catalytic processes

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Catalytic processes play a key role in the petrochemical industry and must be subjected to continuous innovation in order to satisfy the increasing demand for fuels and industrial raw materials, by means of environmentally friendly and energetically efficient technologies. This research group works at the development of catalytic processes by integrating the knowledge acquired at different operation scales, from microscopic scale to industrial implementation. The innovations have been arranged according to an ascending scale order.

## CATALYSTS

**New catalyst preparation** is studied: i) acid catalysts, based on modified HZSM-5 zeolites (steaming, doped with alkaline metals, desilication) and silicoaluminophosphates (SAPOs), with suitable acidity and porous structure for maximizing yields and selectivities, attenuating deactivation; ii) metallic catalysts, based on both noble and transition metals, supported on acid or inert functions ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ); iii) bifunctional catalysts, by combining the former catalysts, using different promoters; iv) core-shell catalysts, via the coating of the metallic function by the acid one; v) ad hoc property catalysts, such as those for  $\text{H}_2\text{O}$  or  $\text{CO}_2$  capture.

**Deactivation and regeneration** of the catalyst plays a main role in their kinetic performance, whose study requires the design of new physicochemical characterization and spectroscopic analysis methodologies for the deactivated catalyst (FTIR, Raman, UV-vis, FTIR-TPO).

## KINETIC MODELLING

The complexity of the reaction scheme of catalytic processes requires progressing in different modelling stages: i) knowledge of the **reaction mechanisms**; ii) proposal of **kinetic schemes** that consider catalyst deactivation; iii) establishment of **kinetic equations** that quantify the effect of all the operating variables; iv) acquisition of kinetic results by means of suitable **reaction and analysis systems**; v) application of effective **methods for experimental and kinetic data analysis** in order to obtain the kinetic parameters. The development of these stages includes common aspects for the different processes, which are carried out by the group on acid, metallic and bifunctional catalysts.

## DESIGN OF NEW REACTORS

The design of catalytic reactors faces new challenges (multiphase processes, high pressure, rapid deactivation of the catalyst, thermodynamic limitations, energy requirements). The innovations carried out by the group include: i) new laboratory scale reactors for **the simulation of industrial operating conditions** (FCC riser simulator, fluidized reactor with catalyst circulation); ii) **new gas-solid contact reactors** (spouted beds), which intensify the reaction by integrating the reactor with separation systems (membrane reactors) and downstream reactors (fixed-fluidized, spouted-fixed); iii) development of **simulation programmes** for laboratory scale, pilot plant and industrial scale reactors, establishing the optimum production strategies, energy efficiency and minimization of emissions.

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# Strategies for catalytic removal of recalcitrant compounds in stationary sources

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KEY WORDS: Chlorinated volatile organic compound, dioxine, furanes, methane, NO<sub>x</sub>, catalytic oxidation

Removal of chlorinated volatile organic compounds (Cl-VOC), dioxins (PCDD), furans (PCDF) and NO<sub>x</sub> that come from stationary sources are studied in this work. These kinds of pollutants are directly or indirectly related to many environmental problems and human health.

From these pollutants, VOCs appear in power generation industries in which, after the combustion remain in the output currents in small concentrations, whereas chlorinated hydrocarbons appear in different chemical industries such as polymers or plastics processing plants among others. On the other hand, PCDD/F and NO<sub>x</sub> appear in solid urban waste (SUW) incinerations plants, where PCDD/F had to be oxidized and NO<sub>x</sub> reduced.

Catalytic oxidation is presented as a good removal technique because the use of a catalyst reduces the operating temperature and directs the reaction towards the desired products compared to thermal incineration. For the suitable functioning of this technique is necessary the selection of an appropriate catalyst with high activity, appropriate selectivity and good stability. Currently, most catalysts used in the industry are based on supported platinum and palladium. These metals exhibit a good activity but have significant disadvantages such as high sensitivity to deactivation by chlorine addition to its high cost and limited availability. An alternative to these materials are metallic oxides. Among these, cobalt oxide, Co<sub>3</sub>O<sub>4</sub>, has demonstrated a high capacity for the total oxidation of chlorinated VOC and CH<sub>4</sub>. The drawback of this oxide is the low stability at high temperatures. To avoid this, one alternative is to use a support or to structure the metal oxide to minimize sintering and improve its catalytic properties. In addition, vanadium oxide has shown good performance on PCDD and PCDF oxidation as well as in NO<sub>x</sub> reduction, both in separated stages in SUW incineration plants.

Our research has been focused on the enhancement of the catalytic properties of cobalt oxide and on finding an alternative catalyst to remove PCDD/F and NO<sub>x</sub> of SUW incineration plants and doing both processes in only one stage.

About chlorinated VOC removal, Co<sub>3</sub>O<sub>4</sub> supported on structured silica SBA-15 has been tested. This kind of support protects cobalt oxide from sintering, because the oxide is introduced in the pores of the silica which avoids the growing of the oxide nanocrystal. Thus, supporting the oxide greater surface area can be obtained, with enhanced the activity of the metal oxide at high temperatures such 400-500 °C. Beside this, Co<sub>3</sub>O<sub>4</sub> can be structured as well. Varying the preparation method some kind of nanorods, nanosheets and nanocubes can be obtained. With this preparations surface area is also enhanced although not as long as with a support, but the redox properties of the sample are quite better because of the absence of a support. So this sample enhanced the activity of the metal oxide at lower temperatures such 200-300 °C because of the more redox sites which are available for the reaction. In both situations It has not been detected any formation of carbon monoxide, due to de strong oxidation power of the cobalt oxide. Finally all the samples have shown less than 10% of activity working long hours.

The research about the oxidation of PCDD/F and reduction of NO<sub>x</sub> of SUW incineration plants has been carried out simultaneously with both pollutants. So, in addition to test for this process the supported vanadium oxide on titanium oxide (VO<sub>x</sub>/TiO<sub>2</sub>), which is used at the industry for both processes separately, we have employed other type of catalysts which also have good activity for both processes separately. We have tested manganese oxide (MnO), manganese and cerium mixed oxide (MnCeO) and copper supported on ZSM-5 zeolite (Cu/ZSM5), prepared by ionic exchange. Manganese oxide and manganese-cerium oxides samples have shown better activity than the VO<sub>x</sub>/TiO<sub>2</sub> samples in the oxidation reaction, and Cu/ZSM5 sample has shown the greater activity in the reduction step. But for both processes simultaneously manganese-cerium oxide has been the sample with the best performance. It has been also shown that for both reactions the active site are the same, as long as when the oxidation starts the reduction goes down. The selectivity is also better for these samples. Due to the less formation of CO with MnCeO sample and the less formation of N<sub>2</sub>O with Cu/ZSM5 sample. Finally, it has been checked that the samples VO<sub>x</sub>/TiO<sub>2</sub> and MnCeO are stable at 300 °C.



# Catalysis for the production of energy and chemical recycling of plastic wastes

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KEY WORDS: Catalysis, H<sub>2</sub> production, APR, WGS, OWGS, CO-PROX, feedstock recycling, plastic wastes.

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The work summarized in this contribution is focused on the use of catalytic technologies for research and development in the field of energy and waste recycling. With this view in mind, the studies cover different lines: chemical recycling of plastic wastes, hydrogen production and hydrogen purification.

## CHEMICAL RECYCLING OF PLASTIC WASTES

Chemical (or feedstock) recycling is one of the alternatives in plastic waste management to prevent landfilling of post-consumer plastics. It covers a wide range of technological processes where the polymer molecules undergo depolymerization and break into smaller molecules. When the wastes are formed by separated and relatively pure condensation polymers, such as polyethylene terephthalate (PET), used in drinking water bottles, depolymerization produces monomers which, after purification, can be used to produce new polymers, ideally indistinguishable of those prepared from the raw materials. In this line, the group has worked with PET and polyurethanes (PU), both pure and from actual wastes, and two technologies: hydrolysis and glycolysis. The solid polymer is kept slurred in the solvent, where the homogeneous catalyst is solved. Depolymerization occurs in the surface of the slurred polymer particles, which decrease in size with time.

Separation of most plastic wastes is usually too costly. Thus, other technologies focus on depolymerization of mixtures to produce fuels. Among them, the group has chosen catalytic hydrocracking of plastic wastes as, in a single stage, a high added value liquid automotive fuel can be obtained. In this process, the polymer is solved in the liquid phase, where a solid catalyst is kept slurred and hydrogen is continuously bubbled. A model catalyst consists of platinum supported on a zeolite, with high external surface area.

## HYDROGEN PRODUCTION AND PURIFICATION

The objective in this line is to develop catalytic technologies promoting the use of hydrogen as the energy vector. With this objective, the group has worked in hydrogen production with different strategies: gas-phase and liquid-phase reforming. Gas-phase reforming includes steam reforming (SR), oxidative steam reforming (OSR) and partial oxidation (POX), depending on the use of steam, oxygen or both, while liquid-phase reforming is focused on aqueous phase reforming (APR). The former can be used to produce hydrogen from any fuel, including methane, gasoline, naphtha or even biomass-derived fuels. APR is oriented mainly to biomass-derived oxygenated compounds such as ethanol or glycerol, and presents the advantage of working at much lower temperatures, although it requires very active catalysts. Nickel-alumina spinels seem to be promising formulations.

Hydrogen produced by the above technologies contains a variable concentration of CO (0.1 - 10 %) that must be reduced to below 50 ppm for its use in proton-exchange membrane (PEM) fuel cells. PEM fuel cells are preferred for mobile or small-scale applications. Removal of CO requires several catalytic steps: high- (HTWGS) and low-temperature water gas shift (LTWGS) followed by preferential oxidation of CO (CO-PROX). Alternatively, LTWGS and CO-PROX can be substituted by oxygen-assisted water gas shift (OWGS). A number of catalytic formulations has been studied, particularly for the low-temperature processes (LTWGS, CO-PROX and OWGS). Copper-containing cerium or cerium-zirconium mixed oxides are, at present, among the best catalytic options.

# Microencapsulation and microwave drying technologies to obtain enriched food material.

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Nowadays, there is a growing interest in food additives, such as vitamins, antioxidants or probiotics, which are added to enrich nutritionally habitually consumed foods (bread, pasta...). In order to reach this goal, microencapsulation techniques are used for protecting the substances to be added. When the substances are microencapsulated, a technology of a microwave drying on a fixed-fluidized is proposed in order to dehydrate thermosensitive materials, allowing a less deterioration, mayor stability and an increase of the lifespan.

Microcapsules are made with 2% of alginate and coated with chitosan, using an extrusion technique called *Jet Cutter*, obtaining spherical microcapsules of about 500  $\mu\text{m}$  diameter. The microcapsules were dehydrated in a microwave drier that consisted of the following essential elements: an air dryer, a heating and cooling air and optical fibers to follow the temperature. A series of experiments were planned with different phases and temperature levels. As consequence of the microwave experiments the most adequate operating conditions could be established. Some of significant benefits derived of microwave drying are as follows:

1. Opposed to the traditional drying in this case, the microwave dehydration takes place from the heat released inside of material due to the water content.
2. An inverse temperature gradient appears favoring moisture removing and promoting the drying of the microcapsules.
3. Compared to conventional systems, the temperature level and the processing times are reduced.

Combination of microencapsulation and microwave drying seems to be a very promising method to obtain enriched foods. From the results of this research the following general conclusions have been obtained:

- The *Jet Cutter* microencapsulation technology enables less deterioration of the encapsulated substance.
- Microwave drying in fixed-fluidized bed gives us a good temperature control and a better product quality over conventional drying.
- In the drying process, three phase characteristics are observed: Phase I is characterized by the removal of surface moisture, in Phase II the diffusional control appears because the water has to emerge from the inside of the material and finally the phase III, which is the final drying stage for removing the remaining moisture.
- This technology reduces drying times easily, reaching the level of moisture content required for product quality control and non-proliferation of microorganisms.
- It is necessary to search for appropriate measures to minimize the deterioration of the heat-sensitive compounds and to enable the kinetics of the process operational strategies.
- Reducing processing times also reduces the energy consumption (cost of the process), which may sometimes be subjected to the quality of dehydration.

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