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Comité editorial: Consuelo Díaz Maroto, Juan Carlos de Haro, Antonio de la Hoz, José Luis Martín, José Fernando Pérez, Javier Torres, Florentina Villanueva.

## PRESENTACIÓN

El número de Junio es un número monográfico dedicado a las jornadas de Ciencia Joven. Este año se ha producido un aumento del número de contribuciones y hay una serie de conferencias de gran interés.

Desde este número la revista tiene ISSN, lo que nos permitirá ampliar la capacidad de publicación. Por ejemplo los resúmenes de Ciencia Joven publicados en este número ya se considera que están publicados en una revista oficial.

Todos esperamos que esto anime a los investigadores a mandarnos cualquier información que consideréis de interés.

El consejo editorial.



## PRESENTACIÓN

### CIENCIA JOVEN

La Facultad de Ciencias y Tecnologías Químicas de la Universidad de Castilla-La Mancha (UCLM) en Ciudad Real ha acogido iernes el simposio Ciencia Joven, durante el que los investigadores noveles presentan sus líneas de trabajo a sus colegas del centro universitario. El encuentro, que cumple su décima edición con un programa ampliado, ha sido inaugurado por el rector de la UCLM, Miguel Ángel Collado, a quien ha acompañado el consejero de Educación, Ángel Felpeto.

Los jóvenes investigadores de la Facultad de Ciencias y Tecnologías Químicas han trabajado intensamente en el desarrollo del décimo Simposio de Ciencia Joven, una iniciativa organizada por ellos mismos que les sirve como plataforma de presentación de sus líneas de investigación y de sus avances. El encuentro ha sido inaugurado formalmente esta mañana por el rector de la Universidad de Castilla-La Mancha (UCLM), Miguel Ángel Collado, quien ha puesto el acento precisamente en el carácter intergeneracional del simposio. “Gran parte del éxito de esta iniciativa se encuentra en el hecho de que propicia la participación de investigadores jóvenes y de otros con una amplia experiencia”, ha explicado el rector, quien también ha elogiado la actividad investigadora y la importante capacidad de transferencia de resultados de la Facultad de Ciencias y Tecnologías Químicas.

Por su parte, el consejero de Educación, Ángel Felpeto, ha manifestado una “total implicación con la Universidad de Castilla-La Mancha” que proviene de su experiencia como director de la extinta Escuela Universitaria de Ingeniería Técnica de Toledo y de la más reciente, como miembro del Consejo Social de la UCLM, en la que cesó tras su nombramiento al frente de la Consejería. “Yo siento a la Universidad de Castilla-La Mancha como mía, y me gustaría que así la sintieran todos los ciudadanos castellano-manchegos, las empresas; que sintiéramos que nuestra universidad marca el futuro de nuestra región”, ha expresado.

#### **Los jóvenes, protagonistas**

El decano de la Facultad de Ciencias y Tecnologías Químicas, Ángel Ríos, se ha referido a la celebración del simposio Ciencia Joven como una excelente oportunidad para los investigadores noveles. “Nuestra intención –ha señalado- era que los jóvenes investigadores fueran los protagonistas de este simposio, así que todo lo hacen ellos, desde la organización del evento a la recepción y selección de comunicaciones, y, lo que es más importante, la presentación de su propio trabajo, sus líneas y sus resultados”.

En el simposio, en el que colabora la Real Sociedad Española de Química, se han inscrito un total de 140 investigadores y se han admitido treinta y seis comunicaciones orales en los distintos ámbitos que abarca la Facultad: Química Inorgánica, Ingeniería Química, Química Orgánica y Química Analítica.

# CIENCIA JOVEN

Entre otras líneas de investigación, durante estos días se está hablando de las propiedades de los aceites vírgenes del pistacho, del tratamiento de los residuos de agua en la industria farmacéutica, de nuevos tratamientos terapéuticos en la lucha contra el cáncer, o de nuevas tecnologías de producción de hidrógeno.

El simposio se completa con la intervención de los prestigiosos investigadores externos José Luis Sotelo y Abderrahmane Boujakhrou, de la Complutense de Madrid; Rachid Salghi, de la universidad marroquí de Ibn Zohr; y José Cernicharo y Raquel Mateos Briz, del Consejo Superior de Investigaciones Científicas.

Gabinete Comunicación UCLM. Ciudad Real, 9 de junio de 2016



## ELIMINACIÓN DE CONTAMINANTES PRIORITARIOS Y EMERGENTES PRESENTES EN AGUAS

José Luis Sotelo

Existe un interés creciente sobre la presencia de contaminantes específicos en concentraciones reducidas en aguas potables y residuales, con miras a incrementar la calidad de las aguas y facilitar su reutilización. La disponibilidad de técnicas analíticas muy sensibles y el desarrollo de métodos terciarios de tratamiento han facilitado su estudio. Estos contaminantes proceden de fuentes diversas, tales como la actividad industrial o agrícola, o la propia actividad humana. Un primer enfoque se centró en los contaminantes procedentes de la actividad industrial, que aunque se



encuentran en concentraciones reducidas tienen en muchos casos fuerte impacto y toxicidad. Así existen leyes que prohíben completamente la incorporación de estos contaminantes a las redes de tratamiento o limitan su vertido. Se han definido asimismo un conjunto de contaminantes prioritarios, presentes en aguas en concentraciones muy bajas pero de elevada toxicidad y persistencia, y dentro de ellos se destaca un grupo por su mayor peligrosidad al ser bioacumulables, existiendo disposiciones que fijan las concentraciones máximas permisibles en aguas continentales y normas para limitar sus vertidos. Por último, se define un grupo de contaminantes emergentes, derivados en su mayor parte de la actividad humana, y presentes en aguas en concentraciones muy bajas, sobre los que no existen todavía normativas, aunque reciben atención creciente y sobre los que se realiza una intensa investigación. Además de los tratamientos biológicos habituales en las plantas de tratamiento, que pueden destruir total o parcialmente algunos de estos contaminantes, el carácter refractario de muchos de ellos, obliga a utilizar tratamientos terciarios adicionales para lograr una destrucción más extensa. Se han desarrollado numerosos tratamientos terciarios que permiten la destrucción en mayor o menor extensión de estos contaminantes. Cada una de estas tecnologías, algunas maduras y ya establecidas y otras todavía en desarrollo, se han aplicado a muy diferentes contaminantes, en condiciones variables, más o menos cercanas a la realidad (nivel de concentración, compuestos puros o mezclas reales). Finalmente, debe contemplarse el objetivo último para la aplicación de estas técnicas. Como ejemplo, se considera la reutilización de aguas residuales, que impone unos niveles de calidad más elevados que los correspondientes al simple vertido de las aguas tratadas a los cauces públicos.



## PHYTOBAC AND ELECTROCOAGULATION: TWO PRACTICAL MANEGEMENT TOOLS FOR PESTICIDES WASTEWATERS

Rachid Salghi

The disposal of pesticide-containing waste is a problem of worldwide concern. With almost every stage of pesticide used involving the formation of wastes [1], that contains substances that are strictly controlled by regulatory bodies. The presence of large stocks of pesticides that are unusable, either due to the fact that they are banned or have expired, is of great concern especially, in developing countries [2]. Various methods for pesticide treatment are available, according to the World Health Organisation which include high temperature incineration, chemical treatment or removal to specially engineered landfill sites [2].



This work provides new results on the electrocoagulation and phytobac degradation of pesticide and lead to the following conclusion such as, after 1 year, the pesticide residue in the pytobac is lower at limit of quantification (LOQ). For all pesticide studied by electrocoagulation the removal of pesticide wastewater is between 95 to 98 %.

### References

- 1 A.S. Felsot, K.D. Racke, D.J. Hamilton, Disposal and degradation of pesticide waste, Rev. Environ. Contam. Toxicol. 177 (2003) 123–200.
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## NANOMATERIALES HÍBRIDOS PARA BIOSENSORES

Abderrahmane Boujakhrou



Durante los últimos años, el desarrollo de biosensores electroquímicos con mejores propiedades analíticas y de estabilidad ha estado estrechamente relacionado con el diseño de nanomateriales de nueva generación. Dentro de este campo, la preparación de nanomateriales híbridos ha recibido especial atención, dado que las propiedades bioelectroanalíticas de estos nanomateriales pueden ser racionalmente predeterminadas a partir de la manipulación de los diferentes materiales

constituyentes. En esta presentación se describen diversas metodologías orientadas a la preparación de nuevos nanomateriales híbridos para su empleo en el diseño de biosensores electroquímicos. Estas estrategias incluyen:

- La preparación de derivados de óxido de grafeno reducido modificado con derivados de polisacáridos hidrosolubles.
- La síntesis de nanohíbridos de grafeno decorado con nanopartículas de oro y brochas de dextrana monofuncionalizada.
- La preparación de materiales híbridos de grafeno y dendrímeros de poliamidoamina.
- El diseño de nanopartículas Janus de oro-sílica mesoporosa para su uso como soporte para la co-inmovilización de enzimas y su empleo en la construcción de biosensores bienzimáticos.
- La síntesis de nanocintas de polímeros de coordinación de plata-bipiridina decoradas con nanopartículas de oro, con actividad intrínseca tipo peroxidasa.

Asimismo, se describe el diseño de un inmunosensor electroquímico, desarrollado en colaboración con la UCLM, para la determinación de *Brettanomyces bruxellensis* en vinos tintos.

## CAFÉ Y CHOCOLATE: DE ALIMENTOS PROHIBIDOS A ALIMENTOS PARA LA PREVENCIÓN DE ENFERMEDADES

Raquel Mateos Briz



El café y el chocolate en forma de productos solubles de cacao, dos de las bebidas más consumidas en nuestra sociedad, son alimentos controvertidos. Sin embargo, estudios de intervención con humanos recientes revelan que su consumo moderado tiene un efecto beneficioso para la salud cardiovascular asociado a su composición rica en fitoquímicos. En el caso del cacao principalmente a través del incremento de la concentración de HDL-colesterol, y en el del café por sus efectos hipotensivos, hipolipémicos, hipoglucémicos y antioxidantes, fundamentalmente,

observándose además una acción positiva sobre la composición corporal. Estos resultados indican que el consumo de estos alimentos es recomendable para la población en general, mostrando el café mezcla tostado/verde beneficios adicionales que permiten su recomendación a personas con sobrepeso o en las primeras fases de la diabetes tipo 2.

## ASTROQUÍMICA: COMPLEJIDAD QUÍMICA EN EL ESPACIO

José Cernicharo



La astroquímica es un campo de investigación bastante reciente de la Astrofísica. En los años 70 se detectaron varias especies moleculares en las nubes de gas y polvo del medio interestelar abriendo así la puerta al estudio de las condiciones físico-químicas de las zonas de formación de estrellas y planetas.

Las moléculas se forman a partir de reacciones bimoleculares iniciadas por los rayos cósmicos en los que la molécula  $H_3^+$  juega un rol esencial. A lo largo de la evolución dinámica de dichas nubes las reacciones de superficie en los hielos que cubren los granos de polvo participan en el aumento de la complejidad molecular en el espacio. Se han detectado unas 180 especies moleculares a través de su espectro rotacional y toda una familia de moléculas todavía mal caracterizadas, pero ubicuas, compuestas por múltiples anillos bencénicos, los llamados PAHs (hidrocarburos policíclicos aromáticos).

En el momento de formación de los discos proto-planetarios la composición del gas y de los granos de polvo van a jugar un papel clave en la formación de planetas, en particular de planetas rocosos como la Tierra.

Se analizarán los procesos químicos que dan lugar a las especies moleculares encontradas en el espacio y se discutirán los procesos de formación de los granos de polvo.

Finalmente se presentará el proyecto Nanocosmos que pretende reproducir en el laboratorio los procesos químicos que dan lugar a la formación de las nanopartículas a partir de las cuales se forman los granos de polvo en las atmósferas de las estrellas gigantes rojas.



## COMPOSITION AND PROPERTIES OF PISACHIO VIRGIN OILS AND ITS BY-PRODUCTS FROM DIFFERENT CULTIVARS

R.M. Ojeda-Amador, S. Gómez Alonso, M.D. Salvador, G. Fregapane

Food Science and Technology

Since several years, particular attention has been given to the dietary consumption of nuts (almonds, pistachios, walnuts and so on) due to their higher content in unsaturated fatty acid, antioxidants and biological active compounds, and thus their possible beneficial health effects. Among nuts, pistachio (*Pistacia vera*) exhibits interesting nutritional value, mainly due to the content of phenolic and tocopherol compounds, which show antioxidant and other bioactive properties. The aim of this work is the characterization of four different pistachio cultivars (Avdat, Larnaka, Kerman and Mateur), their cold-pressed virgin oils and residual

cakes. The chemical analyses were carried out to assess the total and individual phenolic content (by Folin-Ciocalteu and LC-MS), tocopherols (by HPLC) and their antioxidant activity (by DPPH and ORAC). Fatty acids and volatile compounds were measured also in these oils. Furthermore, the sensory properties of pistachio virgin oils have been evaluated, which provide greater value to consumers than refined oils. The present work is a first step to describe the chemical composition of different pistachio varieties. Future work may investigate the effect of roasting and of different operating conditions during cold-press extraction on pistachio virgin oil components.





## CHIRAL N,N,CP-SCORPIONATE ZINC ALKYLs AS EFFECTIVE AND STEREOSELECTIVE INITIATORS FOR THE LIVING ROP OF LACTIDES

A. Otero, J. Fernández-Baeza, L.F. Sánchez-Barba, J. Tejeda, M. Honrado, S. Sobrino, A. Garcés, A. Lara-Sánchez, A.M. Rodríguez  
Inorganic Chemistry



During the last years, our research group has contributed widely in the preparation of efficient catalysts bearing heteroscorpionate ligands derived from bis(pyrazol-1-yl)methane moieties for the preparation of biodegradable polymers by a well-controlled ring-opening polymerization (ROP) of cyclic esters,<sup>1</sup> such as lactide, an inexpensive annually renewable natural feedstock.<sup>2</sup> The biocompatible nature of the polylactides<sup>2</sup> (PLAs) have attracted our attention in the employment of biocompatible metals such Magnesium or Zinc for the design of these catalysts. In this context, whereas a large number of

complexes containing [NNX] (X= N, O, S) heteroscorpionate ligands have been prepared,<sup>1</sup> the [NNCp] hybrid scorpionate/cyclopentadienyl compounds have been, contrarily, little studied.<sup>1,3</sup>

In the present work, we described the synthetic accessibility of the first examples of Zinc metal complexes bearing a racemic hybrid scorpionate/cyclopentadienyl ligand, their different structural arrangements, the reactivity found, as well as their catalytic behavior as single-component initiators for the efficient and stereoselective ROP of rac-lactide in the production of heterotactic-and isotactic enriched polylactides.

### References:

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2. For reviews in this area see for example: (a) Cameron, D. J. A.; Shaver, M. P. *Chem. Soc. Rev.* 2011, 40, 1761-1776. (b) Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* 2010, 43, 2093-2107.
3. Honrado, M.; Otero, A.; Fernández-Baeza, J.; Sánchez-Barba, L. F.; Lara-Sánchez, A.; Tejeda, J.; Carrión, M. P.; Martínez-Ferrer, J.; Garcés, A.; Rodríguez, A. M. *Organometallics* 2013, 32, 3437-3440.

## WASTEWATER MANAGEMENT IN THE PHARMACEUTICAL INDUSTRY

J.F. Pérez, C. Sáez, J. Llanos, C. López, P. Cañizares, M.A. Rodrigo

Chemical Engineering



The primary objective of the pharmaceutical industry is to produce substances that have therapeutic value for humans and animals. Those industries make use of a vast array of complex batch-type processes and technologies in the manufacture of pharmaceutical products. With this diversity of processes comes a similarly diverse set of waste streams, including aqueous effluents. In particular, wastewater generated in organic-synthesis pharmaceutical plants are complex and highly toxic, mainly containing: organics (remaining reagents, reaction products and by-products, solvents) and ionic compounds

(reagents, acids/bases) resulting in both high COD and salinity levels. Due to the diversity of characteristics of those effluents, there is not a single technology which meets all the requirements from every industrial facility. Because of this, wastewater treatment from pharmaceutical facilities requires an intensive research in order to develop the most appropriate processing sequence. In this context, a close collaboration with a pharmaceutical company from Castilla-La Mancha is in progress. First part of the project consisted in sampling and analyzing every waste stream generated in the facility (approximately 160 samples). Next, a technological screening was conducted for testing a wide range of technologies for the treatment of the aforementioned wastewater. With all this information, an optimal management strategy was developed. At the same time, some of the electrochemical alternative of the technologies applied during the screening are under study. In particular, a novel and cost-effective electro-fenton reactor is currently being developed. Preliminary tests indicate that this design could mean a great leap in the development of the electro-fenton technology.

## THE METABOLIC RESPONSE TO INGESTION OF A BOLUS OF FAT IS CONDITIONED BY THE AGE

A. Fernández, N. Gallardo, A. Andrés

Biochemistry

Excess of ingested fat may be converted in glucose, but this process will take hours. However, fat intake itself have a considerable impact on postprandial glycemia for two reasons: 1.- Fats meal delayed gastric emptying, thereby delaying the digestion and absorption of carbohydrates, and consequently the increase in blood glucose after food intake. 2.- Fats impairs insulin sensitivity, and this condition is maintained for hours. Decreased insulin sensitivity lead to increased hepatic glucose production and / or decreased insulin-mediated glucose uptake. However, insulin-independent mechanisms for glucose lowering also account for glucose



disposal. Thereby, increasing our current knowledge on the role of fat meal on postprandial glycemia will be of great relevance for diabetics in order to adjust the proper dose of hormone during insulin therapy. Increasing age is a major risk factor for the development of type 2 diabetes, thus, we hypothesize that ageing is associated to changes in lipid metabolism in the postprandial state that cause postprandial hyperglycemia. To this end we performed an oral fat tolerance test. The experiment was conducted in 3-, 8- and 24-months-old Wistar rats. Overnight fasted rats were administered a bolus of virgin olive oil intragastrically (1 mL/Kg of body weight) and blood samples were taken from the tail vein before the fat load ( $t = 0$ ) and 30, 60, 90, 120, 180 and 240 min after fat administration. Blood glucose, triacylglycerides and total cholesterol were determined immediately using an Accutrend Glucose Analyser (Roche). Blood samples were centrifuged and plasma was frozen at  $-70^{\circ}\text{C}$  until FFA, ketone bodies, insulin, leptin and FGF21 estimation. Overall changes in lipids, glucose and insulin during the test were calculated as the area under the curve above the basal level. In addition we measured the expression of several genes involved in lipid and glucose metabolism in both liver and adipose tissue. We found Age-Related Differences in postprandial metabolic profile and liver and adipose tissue response to fat intake. Aged rats need more insulin to maintain postprandial normoglycemia, nevertheless, hyperglycemia occurs at 240 min after fat administration. We suggested that the impairs in glucose homeostasis observed in aged rats after a fat meal occurs via insulin-dependent and insulin-independent mechanisms.



## DETERMINATION OF BIOMOLECULES BY CHEMILUMINESCENCE IMMUNOASSAY (CLIA)

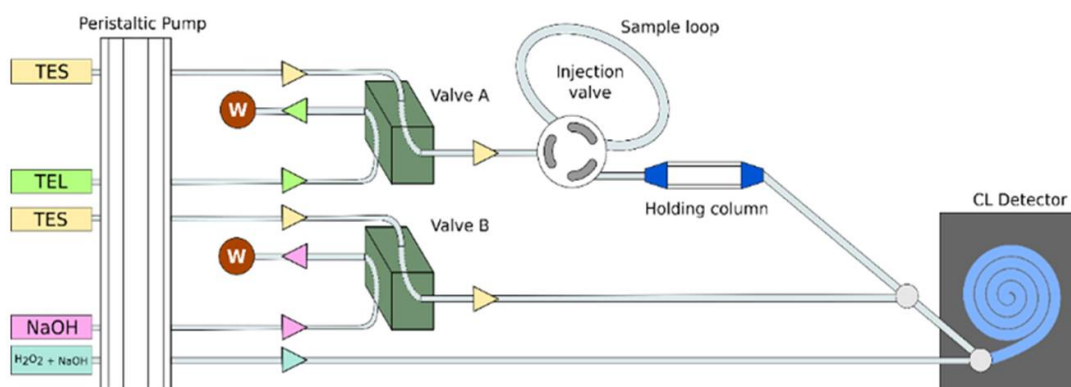
J.A. Murillo, A. Alañón, E. Jiménez

Analytical Chemistry



Mycotoxins are toxic compounds produced as secondary metabolites by fungi. These toxins are highly hepatotoxic, nephrotoxic, teratogenic and mutagenic to most mammalian species. They have also shown carcinogenic effects in humans. On the other hand, the impact of the food allergies in the society has presented important challenges for both, the clinical allergology and the food industry. That reason, the information of the presence of allergens should be considered as mandatory in the labelling of foods and it is of great importance to develop fast, low cost analytical methods with high selectivity and sensitivity. In this study, in addition to the determination

of mycotoxins, it is proposed the analysis of various allergens (water-soluble proteins or glycoproteins), since in recent years consumers are demanding more information about the foods we eat. It is intended to use a specific recognition element, locking systems such as gels and new materials including modified and magnetic nanoparticles and nanotubes. For this purpose, a new assembly has been designed consisting of simple and economical immunoassay techniques adapted to a flow injection system and chemiluminescence detection. The initial scheme designed for the method is shown below. As an initial task in a new line of work we have tried to understand and manage the steps involved in the immunoassay, such as the anchor of the antibody on the support, the labeling of the chemiluminescent molecule with the antigen and the quantum efficiency of such molecule. The resulting methodologies will be validated by comparison with official methods or those described in the scientific literature to demonstrate the advantages of the developed procedures and the new instrumentation.





## SMART SELF-HEALING HYDROGELS BASED ON GRAPHENE

C. Martín, S. Martín, M. Prato, E. Vázquez

Organic Chemistry

Inspired by nature, self-healing materials<sup>1,2</sup> represent one of the vanguards of recent developments in the synthesis of new smart materials. All natural or synthetic materials accumulate damage at macro or microscale, losing even the function of the device due to the deterioration or disappearance of their desirable properties. However, self-healing materials can reverse or repair the damage zone once or several times because they are able to recover their capabilities. This fact enhances the lifetime of these kinds of materials. There is a multitude of strategies used to synthesize self-healing gels. Overall, the chain diffusion at the interface of the damaged region was considered to be

the primary driving force for repairs. Therefore, semi-interpenetrating polymer networks (semi-IPNs) are one of the best candidate materials to reach that goal. Here, autonomous self-healing capacity has been achieved in different novel composite hydrogels. The materials are synthesised by several strategies depending on the desired structure. Thus, the healing efficiency of both copolymers and semi-IPNs based on oppositely charged polyelectrolytes is studied and compared. Moreover, graphene with almost no defects<sup>3</sup> is also used as filler in some cases. The healing efficiency is corroborated not only by SEM analysis of the damaged/healed region, but also by tensile experiments. All the materials have excellent self-healing ability, reaching almost the 100% of healing in some cases, in which real free chains are able to diffuse through the interface, guided by existent ionic interactions. In addition, the presence of graphene into the polymer network improves the conductivity of the final composites.



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## ANIMAL WASTE VALORIZATION THROUGH THERMOCHEMICAL PROCESSES

M. Fernandez-Lopez, J.L. Valverde, L. Sanchez-Silva

Chemical Engineering



In this century, the depletion of fossil fuel reserves has been associated to the growing energy demand which has caused, simultaneously, severe environmental problems, including air pollution, global warming and acid rain. For this reason, renewable energies offer a good alternative to solve these drawbacks since they are a never-ending resource to human scale. Among the different renewable energy sources, biomass seems to be one of the most viable routes for the production of clean energy and chemical products. Specifically, livestock biomass is

generated from animal fats, carcasses and excrements, being this animal waste known as manure. The accumulation of livestock manure (LSM) has associated some hygienic and environmental problems due to its high potential for pollution and production. Moreover, traditional uses of livestock manure (LSM) as fertilizer have to be changed due to land limitations and strict regulations. Therefore, the valorization of the manure surplus for bioenergy generation could be a sustainable choice since it is considered a zero-cost feedstock. Generally, the conversion of LSM into energy could be carried out through biological or thermochemical processes. One of the most common biological processes is the anaerobic digestion (AD), resulting in the generation of biogas and a residual digested. Concerning the thermochemical conversion routes, in this work, three thermochemical processes have been proposed for the valorization of LSM: pyrolysis, combustion and gasification processes. Thermogravimetric analysis (TGA) has been widely used for the study of these thermochemical conversion processes. In the present work, the pyrolysis, combustion and gasification processes of different manure samples were investigated by means of TGA coupled with mass spectrometry analysis (MS), being the latter the only one able to afford real-time and sensitive detection of evolved gases

## NEW FERROCENYL DERIVATES AS POTENTIAL DRUGS FOR BREAST CANCER TREATMENT

B. Díaz de Greñu, M.C. Carrión, F.A. Jalón, B.R. Manzano

Inorganic Chemistry

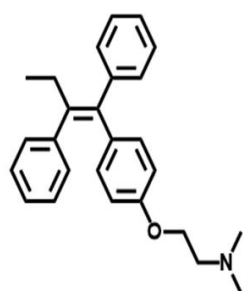


Breast cancer causes cells in the breast tissue to change and grow in an uncontrolled way. It is the most common female cancer (less than 1% of all breast cancer cases affect men) and the second most common cancer overall, causing around 15% of female cancer deaths around the world.<sup>1</sup> Estrogens, the major hormone involved in the biology of breast cancer, bind to receptors in cells which cause cells to divide. Therefore tumour growth can be prevented by controlling the supply of estrogens to the breast tumour, either blocking the receptors or by inhibition of estrogens production. The former case is accomplished by

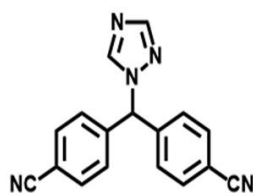
drugs such as Tamoxifen, a prodrug that competes with estrogens for binding to the active site of estrogen receptors in cells. The latter case is conducted by the inhibition of the enzyme aromatase by drugs like Letrozole, thus reducing the amount of estrogens in the body. During the last decade, Jaouen et al. found that the incorporation of a ferrocene moiety to Tamoxifen resulted in improved properties when compared to the initial drug.<sup>2</sup> During this talk the synthesis of new Letrozole analogues containing a ferrocenyl group (generically called Ferrozoles) will be presented, which are expected to show better properties than those achieved with previous aromatase inhibitors.

[1] Available on the internet from: <http://globocan.iarc.fr>, accessed on 12/05/2016.

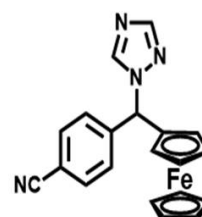
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Tamoxifen



Letrozole



Ferrozole



## VALORIZATION OF BY-PRODUCTS DERIVED FROM THE VINE BY ULTRASONIC-ASSISTED EXTRACTION

L. Marchante, S. Gómez-Alonso, M.S. Pérez-Coello, M.C. Díaz-Maroto

Food and Science Technology

The valorization of winemaking by-products generates great interest to the food, cosmetic and pharmaceutical industries, due to their potential as a source of bioactive compounds. Nowadays, the use of winemaking by-products to obtain different functional ingredients is subject of numerous studies, where conventional extraction methods using organic solvents are used. These extraction techniques produce high pollution, so the development of alternative and clean methods, as ultrasound-assisted extraction (UAE), is required. In this sense, the aim of this work is to obtain rich-phenolic extracts from winemaking by-products by UAE,

as a natural source of antioxidants. The optimum conditions for the maximum extraction of total polyphenols were estimated by means of the application of response surface methodology. The experimental design was applied only to grape marc, using ethanol-water as solvent in a solid/liquid ratio of 1:4, and performing two extraction cycles for 3 min. The best conditions to obtain rich-polyphenol extracts were 44 % of ethanol and 81 % of amplitude. Determination of the total polyphenol content was performed by the Folin-Ciocateu and the antioxidant capacity was evaluated by the method of capturing free radicals using the DPPH radical (2,2-diphenyl-1-picrylhydrazyl) and by the method of the inhibitory activity of the ABTS radical cation (2,2-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid). Among the raw materials studied were included grape marc, seeds and stalks from *Vitis vinifera* L. Cv. Tempranillo. Also, fresh samples were compared with those drying at 45 °C, observing that the oven-drying caused a reduction of the total polyphenol content and antioxidant activity. The results show that extracts of grape marc, seeds and stalks obtained by UAE are an important source of antioxidants, and could contribute to the recovery of waste from the wine industry.





## THE ROLE OF QUANTUM DOTS FOR THE DEVELOPMENT OF ANALYTICAL METHODOLOGIES

G. Durán, A.M. Contento, A. Ríos

Analytical Chemistry



Currently, the use of nanomaterials as analytical tools is one of the most exciting trend in (bio)chemical analysis, providing new opportunities in the development of innovative approaches in the different steps of the analytical process. In this context, a clear example is the use of "quantum dots" (QDs) nanoparticles. The growing importance of this type of nanoparticles as tools in nanoscience and nanotechnology resides in their exceptional optoelectronic properties at nanoscale range due to "quantum confinement" effects and its very

reactive surface. These features confer many of the interesting and, sometimes, unexpected properties of QDs.<sup>1</sup> Due to their exceptional optical properties, QDs have found vast applications in analytical research as the next generation fluorescent probes and new sensing assays. Therefore, QDs are now involved in many analytical applications as analytical tools. In this way, the aim of this communication is to show several analytical procedures for the synthesis, modification and solubilization of CdSe/ZnS QDs, and their subsequent use as analytical tools, contributing to improve the detection and then the determination of compounds of interest in the several fields, such as environmental,<sup>2</sup> food<sup>3, 4</sup> and clinical.<sup>5</sup> Moreover, given the opportunities that they offer in the Analytical science, the development of other compositions of QDs as efficient alternative to conventional semiconductor QDs is being studied.

Acknowledgements: Financial support from MINECO (CTQ2013-48411-P) and JCCM (PEIC-2014-001-P) is gratefully acknowledged.

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## DIRECT SYNTHESIS OF HIGH QUALITY LIQUID FUELS THROUGH FISCHER-TROPSCH PROCESS

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Chemical Engineering



It is well known that the vast world energy demand comes from fossil fuels use. However, energy supply security concerns, air pollution, and global climate change provide incentives for introducing alternative energy carriers to petroleum products. One of the promising candidates is clean and sustainable synthetic automotive fuels produced by Fischer-Tropsch synthesis (FTS). This process has received increasing attention worldwide as can be produced from any carbonaceous feedstock, such as coal, natural gas (including stranded gas), or biomass, and also due to technical advances.

Concept consists of independent, stand-alone facilities, integrated in a gasification combined cycle (IGCC) power plant, where syngas from the IGCC is routed to the FTS plant. Among the possible active phases, cobalt based catalyst provides high activity, selectivity to linear paraffins and stability toward deactivation by water. However, it is important to note that FTS catalytic performance is strongly influenced by the nature of support, metal dispersion, basicity and preparation method. In this sense, the nature of precursor has been investigated. In addition, the effect of basic promoters such as alkali-earth oxides has been studied, resulting in an important shift towards long chain hydrocarbons. Regarding catalytic support, silicon carbide, which is one of the most advanced ceramic materials, has been demonstrated to be an excellent support in such exothermic reaction due to its remarkable chemical and thermomechanical properties. However, FTS process generates a wide hydrocarbon spectra imposed by Anderson-Schulz-Flory distribution. Therefore, along with an efficient FTS catalyst, additional downstream upgrading and separation steps are required to increase selectivity toward commercial middle distillates. In an effort to improve process performance and cost-effectiveness, the possible integration of both FTS and hydrocracking in one-step through a cascade system has been tested, resulting in the direct and complete conversion to valuable fuels.

## SIGNALING PATHWAYS AFFECTED IN ALZHEIMER'S DISEASE HUMAN BRAINS

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Health Science

Alzheimer's disease (AD) is the main neurodegenerative disease in aging. It is the most common dementia that affects to 24 millions of people around the world. AD is characterized by cognitive, behaviour and memory alterations. In human brain, it has been found neurofibrillary tangles with abnormal phosphorylated tau proteins, and deposits of  $\beta$  amyloid caused by aberrant cleavage of its precursor. Adenosine receptors are G-protein coupled receptors distributed in the Central Nervous System. They can inhibit or stimulate adenylyl cyclase



activity, mediating different physiological responses in cells, and have a neuroprotective role. It is also known that protein kinase A (PKA) is implicated in learning and memory processes. Previous results of our group showed that adenosine A1 and A2A receptors are significantly increased in plasma membranes from frontal cortex brain in AD. The aim of the present work was to study different components of transduction pathway in the same cortical area. To this end, cytosolic fraction of post-mortem frontal cortex brain from different stages of AD patients and age-matched controls were extracted. PKA and PKC activities were determined by ELISA. PKC activity was significantly increased from early stages of AD (I-II of Braak). However, PKA activity revealed a biphasic profile decreasing in early-medium and increasing in advanced stages of AD. A1 and A2A receptors analysed by Western-blot were both significantly increased in early stages of AD and AC1, the main isoform coupled to these receptors, was also increased in the same stages. Moreover,  $\beta$ A1-40 was significantly increased from early stages while  $\beta$ A1-42 was increased only in advanced stages in AD. These results show modulation of transduction pathways mediated by adenosine and suggest A1 and A2A receptors, PKA and PKC as promising pharmacological targets in AD.



## NMR MICRO-COILS AS AN ALTERNATIVE FOR CHEMICAL PROCESSES MONITORIZATION

J.M. Mateo, R.M. Sánchez, A. de la Hoz, A. Velders, A.M. Rodríguez, A. Juan, M.V. Gómez  
Organic Chemistry



NMR spectroscopy is one of the most powerful techniques for structural determination. Nevertheless, its main disadvantage is the low sensitivity. One of the possibilities to improve the NMR sensitivity (SNR) is the employment of micro-coils integrated in the surface of the so-called NMR micro-chips (Figure 1), as SNR is inversely proportional to the coil diameter.

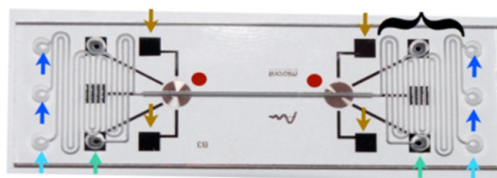


Figure 1. NMR micro-chip with planar micro-coils.

NMR micro-chips are very useful not only for being employed as micro-reactors but also for permitting micro-fluidic connections in order to carry out chemical processes in continuous flow mode. Taking into consideration this approach, we have coupled different chemical activation sources to the NMR spectrometer such as conventional heating,<sup>1</sup> microwave irradiation<sup>2</sup> and photochemistry<sup>3</sup> for monitoring several chemical reactions both inline and in situ detection.

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## NEW APPLICATIONS OF ION EXCHANGE RESINS IN ENOLOGY

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Food Science and Technology



Since the mid-twentieth century the technology of ion exchange resins has been using in the wine industry. Nowadays, ion exchange resins are mainly constituted by a crosslinked polymer matrix on which covalently bind ligands with net electrical charge.

In recent years, dozens of studies have shown the potential that have the ion exchange resins for the removal of oxidizable and oxidized compounds in musts and wines. For this reason, it is necessary to investigate this technology to produce quality wines at a lower cost for the winery.

This study aims at the reducing the concentration of phenolic compounds in white wines using anion-exchange resins without modifying the aromatic complexity and gustatory sensations.

On the experiences made, all the hydroxycinnamic acid derivatives, including free caffeic and p-cumaric acids and their respective esters with tartaric acid, (i.e., caftaric and cutaric acids), drastically decreased after the resin exchange treatment.

## NEW TECHNIQUE TO PRODUCE HYDROGEN: ELECTROCHEMICAL REFORMING OF ALCOHOLS

A.B. Calcerrada, A.R. de la Osa, F. Dorado, A. de Lucas-Consuegra

Chemical Engineering



Nowadays, hydrogen has attracted great interest as a future clean fuel for combustion engines and fuel cells. There are different processes to obtain hydrogen from a variety of materials. However, most hydrogen in the industry was produced by steam reforming of methane. Nevertheless, in the last years the electrochemical reforming of alcohols is developing as a new technique in order to obtain pure hydrogen and is based on the use of electrical power to split the chemically-bonded species by the electro-oxidation of the alcohol fuel. This process can take place in a Proton Exchange Membrane (PEM) electrolysis cell

where the organic compound is supplied to the anodic chamber, and the hydrogen was obtained in the cathodic chamber (Figure 1).

This technique has some interesting advantages as:

- Lower reaction temperatures (<100 °C) than catalytic steam reforming.
- Direct pure hydrogen production, separated from other reaction products.
- Easier and fast control of hydrogen production rate.
- Lower power demands than water electrolysis, since part of the energy required is provided by the organic molecule.

On the other hand, the electrochemical reforming of alcohols also presents some drawbacks as:

- It is an immature technology.
- Limited practical experience.
- Required development of more active catalyst anode and more stable membranes.
- High cost anodic catalyst typically based on Pt-Ru/C.

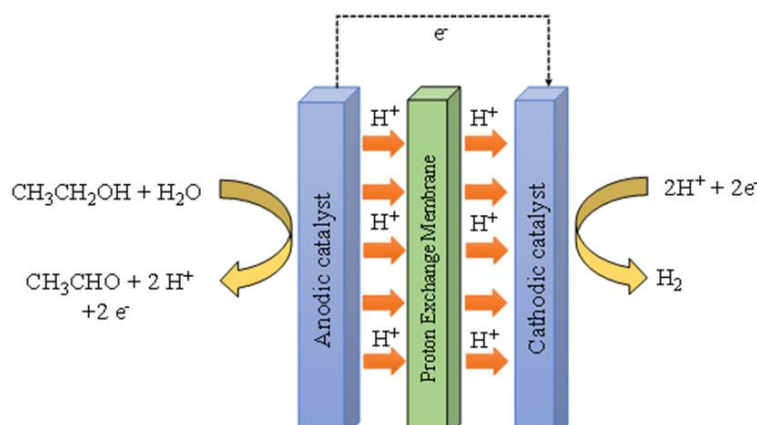


Figure 1. Schematic representation of the set-up used for the ethanol electro-reforming



## DIALKYLBORON GUANIDINATES: SYNTHESIS, STRUCTURE AND CARBODIIMIDE DE-INSERTION REACTIONS

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Inorganic Chemistry



Guanidinate anions are highly versatile and readily accessible ligands, which have been used in recent years as an alternative to cyclopentadienyl-based ligands coordinated to metals and main group elements with emerging applications in catalysis and materials science. The most common synthetic routes to access guanidinato compounds are: (i) insertion of carbodiimides in M-N bonds, (ii) deprotonation of guanidine with a metal alkyl, (iii) salt-metathesis reactions between a metal halide substrate and an alkali metal guanidinate.<sup>1</sup> Within

this family of compounds, examples of boron guanidates are scarce and most of them bear only halide substituents on boron. Thus, we turned our attention to the preparation of novel dialkylboron guanidates through salt methathesis of “in situ” generated lithium guanidates of the formulas  $\text{Li}[(\text{Me}_2\text{N})\text{C}(\text{NR}'_2)_2]$  ( $\text{R}' = \text{iPr}, \text{Cy}$ ) or  $\text{Li}[(\text{iPrHN})\text{C}(\text{NiPr})(\text{NAr})]$  ( $\text{Ar} = \text{Ph}, 4\text{-Me-C}_6\text{H}_4, 4\text{-tBu-C}_6\text{H}_4$ ) with chloroboranes  $\text{ClBR}''_2$  ( $\text{R}'' = \text{Cy}, \text{Norbornyl}$ ) to give compounds  $(\text{Me}_2\text{N})\text{C}(\text{NR}'_2)_2\text{BR}''_2$  and  $[(\text{iPrHN})\text{C}(\text{NiPr})(\text{NAr})]\text{BCy}_2$  in fairly good yields. The solid-state structures of some of these species were confirmed through single-crystal X-ray diffraction analyses. Unexpectedly, we found that the symmetrical boron guanidates undergo de-insertion reactions in solution, even at room temperature, to give the corresponding aminoboranes,  $\text{Me}_2\text{NBR}''_2$ , and carbodiimides,  $\text{C}(\text{NR}'_2)_2$ , which are in equilibrium with the parent guanidates. However, the asymmetrically-coordinated guanidato derivatives turned out to be more robust and only showed evidence of this type of reactivity at higher temperatures.

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## PHENOLIC COMPOSITION OF RED WINES ELABORATED FROM MINOR GRAPE CULTIVARS FROM THE SPANISH REGION OF LA MANCHA

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Food Science and Technology



The vine culture for winemaking is currently dominated by a relatively low number of worldwide spread grape cultivars. However, there are a large number of local or minor grape cultivars whose composition and potential to produce high quality wines have not been properly studied. The phenolic composition of red wines elaborated from little known red grape cultivars, namely Garnacho, Moribel, Benedicto, Mocatel Negro, Tinto Navalcarnero and Tinto Fragoso, which are native from the Spanish region of La Mancha (ca. 450,000 ha of vineyards), have been studied in the 2014 season with the aim

of evaluate the enological potential of these minor grape cultivars. Individual phenolic compounds (anthocyanins, flavonols, hydroxycinnamic acid derivatives and flavan-3-ols) were determined by HPLC-DAD-ESI-MS/MS following methods previously described by our group.<sup>1, 2</sup> The red wines studied had total anthocyanins contents in a similar range to the red wines made from world-renowned Cabernet Sauvignon, Tempranillo, etc., being Tinto Fragoso the richest one. Regarding flavonol profiles, the 3-glucosides of the six common aglycones were found and Tinto Fragoso wines showed higher flavonol concentrations than the others. Hydroxycinnamic acid derivatives (HCADs) showed the characteristic profile of *V. vinifera* wines, being caftaric acid the main HCADs. Tinto Navalcarnero wines had the lower flavan-3-ol monomers and proanthocyanidins contents.

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## BIOMASS AS A RENEWABLE ENERGY RESOURCE. NEW METHODOLOGIES FOR CONVERSION OF LIGNOCELLULOSIC WASTE INTO BIOFUEL PRECURSORS

A. Lorente, C. Lucas-Torres, M.P. Sánchez-Verdú, A. Moreno  
Organic Chemistry



Fossil fuels reserves are decreasing and its use causes high CO<sub>2</sub> emissions. Lignocellulosic biomass has been recognized as the most promising renewable resource for the production of high value bio-chemicals, for instance 5-hydroxymethylfurfural (HMF) and levulinic acid (LA). Our research group works on agrofood and lignocellulosic residues focusing on their carbohydrate contents. Six-carbon carbohydrates are dehydrated in acidic medium at high temperature to obtain HMF and LA, which are interesting compounds as they involve the obtaining renewable precursors for the production of

plastics and biofuels. Considering that, the aim of this work involves the carbohydrate dehydration from beer bagasse, which is generated in beer industries. Thereby environmentally-friendly techniques, such as microwave radiation as energy source, will be used meeting some of the Green Chemistry Principles. Thermogravimetric analysis (TGA) allow us to characterise beer bagasse and NMR spectroscopy provides a tool for the identification and quantification of these “platform” compounds and compare these results when the dehydration is carried out under conventional heating.

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## SEPARATION TECHNIQUES COUPLED TO ICP-MS FOR THE DETERMINATION OF GOLD NANOPARTICLES AND DISSOLVED GOLD SPECIES IN CULTURE MEDIUM AND CELLS

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Analytical Chemistry

In the last decades, the use of gold nanoparticles (AuNPs) has rapidly increased with applications in biomedicine and sensing devices. At the same time, there is also a growing concern about their potential toxicity on biological systems. Nanotoxicity test in vitro with cells are applied to evaluate this risk but the formation of protein coating around the NPs and the liberation of ions may impact the biological response. In order to obtain a correct interpretation of the toxicity results, methods to detect and characterize AuNPs in culture medium and cells are an urgent need. For this purpose, the use of separation techniques coupled to inductively coupled plasma mass spectrometry (ICP-MS) is a promising option. Thus, the aim of this study was to compare two hydrodynamic separation techniques, such as reversed-phase liquid chromatography (HPLC) and asymmetric flow field flow fractionation (AF4), coupled ICP-MS, for the study of AuNPs and dissolved species in culture medium (DMEM) and cells (HeLa) used in cytotoxicity tests. In this work, liquid chromatography allowed the separation of gold species ( $\text{Au}^{3+}$  and AuNPs of different size) in a single chromatographic run using phosphate buffer modified with sodium dodecyl sulphate as mobile phase. The matrix had a significant impact on the behaviour of both  $\text{Au}^{3+}$  and AuNPs. In the case of 10 nm AuNPs, a shift towards minor retention time was observed after a 24 hours incubation period in the culture medium, which suggests a "protein corona" effect. Moreover, methodology based on AF4 has been applied for the detection and characterization of AuNPs in DMEM and an increment in the size distribution was observed, which can be associated with protein corona. Besides, the detection of  $\text{Au}^{3+}$  released from AuNPs in DMEM has been confirmed by both separation techniques.

Acknowledgments: Project MINECO CTQ-2013-48411-P and predoctoral contract MINECO BES-2014-069095, and project PEIC-2014-001-P from Junta de Comunidades de Castilla – La Mancha.



## VOLATILE AND SENSORY PROFILE OF VERDEJO WHITE WINES TREATED WITH OAK CHIPS AT DIFFERENT WINEMARKING STAGES

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Food and Science Technology



This paper reports on a complete study of the effect of wood, in the form of oak chips, on the volatile composition and sensory characteristics of Verdejo wines added at different stages of the fermentation process. Verdejo control wine was made following traditional winemaking process, without oak chips. Oak chips were added to the rest of the wines in one dose rate (7 g/L) at two different stages of the winemaking process: during alcoholic fermentation (AF) and post-fermentation in contact along one week (wine maturation). Aroma compounds were analyzed by Gas Chromatography–Mass Spectrometry (GC–MS). Sensory profile was evaluated by experienced wine-testers. Wines fermented with oak chips during alcoholic fermentation showed higher concentrations of the ethyl esters of straight-chain fatty acids, ethyl, hexyl, isoamyl acetates and superior alcohols than control wines. The highest concentrations of benzene compounds, oak lactones and furanic compounds were found in both wines in contact with oak chips but wines treated with oak chips after alcoholic fermentation presented less concentration of these compounds. It is clear that the use of wood chips gives rise to a different sensorial profile of wines depending at what point of the winemaking process the chips are added. Verdejo control wine presented a sensory profile characterized by fruity, fresh, green apple, citrics, green y tropical fruit notes. Higher intensities of woody, coconut, vanilla, toasty and toffee descriptors are obtained when a large dose rate of chips is employed. All these treatments with oak chips provide another alternative to traditional winemaking methods as its use gives rise to improve and enhance the chemical and sensory profile of wines depending of the point of addition.



## PREPARATION OF PLATINUM COMPLEXES AS ANTICANCER AGENTS

S. Blázquez, M.C. Carrión, B.R. Manzano, F.A. Jalón

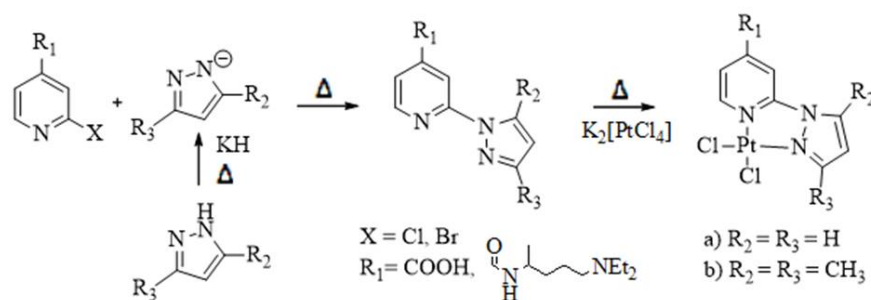
### Inorganic Chemistry

Fighting against cancer is one of the subjects in which many scientists spend a lot of time of their research. Many different drugs, which have shown therapeutic activity against cancer, have been developed during the latest years. Nevertheless, the high reactivity of these molecules, together with their low selectivity and the resistance acquired by some cells, are the main problems of these treatments. Many of these molecules are based on Pt(II). They exhibit cytotoxic activity and they are commonly used in chemotherapy. Cisplatin is the most used drug for tumor treatments —lung, ovary, head and neck.<sup>1</sup> — The widely accepted mechanism

consist on the binding of the complex of Pt (II) to the strands of DNA. By this union, the cellular death by apoptosis is triggered. The lack of selectivity of cisplatin and other drugs, targeting both healthy and cancer cells, causes a huge number of negative side effects. The purpose of this research is the synthesis of new complexes that exhibit similar or higher cytotoxicity, but with an improved selectivity against cancer cells. In the first place, N,N-chelating ligands are combined with substituents that improve the transport of the drug through the cell wall. The subsequent step would be the oxidation to the less toxic Pt (IV) to get the reduction to Pt (II) in the cancer cells. This would reduce the side effects increasing the selectivity.

Knowledgements: MINECO grant (CTQ2014-58812-C2-1-R) and Programa Propio UCLM for financial support. S.B. thanks the Programa Propio for a Master fellowship.

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## PRECONCENTRATION STRATEGIES WITH NANOPARTICLES IN BIOLOGICAL SAMPLES FOR ANALYSIS BY CAPILLARY ELECTROPHORESIS

I. Lizcano, J. Rodríguez, G. Castañeda

Analytical Chemistry



An analytical process usually has several steps, such as sampling, sample preparation, separation, detection, data handling and treatment, to offer the required results. Of these steps, sample preparation might be the most important when target analytes are in complex matrices or direct analysis is not practical due to the lack of selectivity and sensitivity. Numerous potential interferences and low concentrations of analytes make a previous extraction procedure, which usually involves isolation and enrichment of the analytes, necessary. Among different

separation and preconcentration techniques, solid phase extraction (SPE) together with precipitation are the most common because they are simple and faster operation. The development of new extraction techniques and improvement of existing techniques using novel extraction materials are the main trends in this research area. Regarding the latter issue, nanomaterials are promising tools. In this work we have used different methods of pretreatment of the serum sample in order to preconcentrate or eliminate interference that is presented at the time of the determination by Capillary Electrophoresis (CE) of two oncologic compounds (Dabrafenib and Trametinib) simultaneously used in the treatment of cancer skin. It has made a comparative study of classical extraction techniques, such as precipitation or solid phase extraction (SPE) and extraction with different nanomaterials such as, magnetic nanoparticle modified with SDS or multi-walled carbon nanotubes, single carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Of the different pre-treatment systems, the MWCNT has been showing as the better strategy, these materials were characterized by their high surface areas, and they could absorb molecules via non-covalent force, such as hydrogen bonding,  $\pi$ - $\pi$  stacking, electrostatic forces, Van der Waals forces and hydrophobic interactions

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## PESTICIDES REMOVAL WITH AEROBIC ACCLIMATED BACTERIAL CULTURE

B. Carboneras, J. Villaseñor, F.J. Fernández-Morales

Chemical Engineering

Nowadays pesticides are essential for the correct development of crops. The use of pesticides have caused many environmental problems such as increased soil fertility loss, soil acidification, increased weed species resistance and loss of biodiversity. These chemicals can generate problems in living organisms, including humans. Because of the problems described, it is important to develop techniques in order to minimize the effect of pesticides. One of the methods that can be used takes advantage of the ability of microorganisms to remove pollutants. In this context, the aim of this work was to evaluate the aerobic



biodegradability of a commercial herbicide solution, based on oxyfluorfen. The experimental system used in this work consists of batch reactors. The reactors have a continuous shaking and operated at a constant temperature. The volume of each reactor is 500 ml and they are open to the atmosphere in order to allow the oxygen transfer from the atmosphere to the liquid bulk. Different concentration of oxyfluorfen, ranging from 84 to 495 ppm, and different temperatures, ranging from 15 to 30°C were studied. In all the cases, the length of tests was 72 hours. In order to ensure the availability of trace minerals, a nutrient solution was added to the experiments. In previous researches, it was observed the existence of a lag phase in biodegradability studies of halogenated pesticides. For this reason, an acclimated bacterial culture was used in this experimentation. The evolution of the pesticide, the biomass concentration and the total organic carbon (TOC) were analyzed along all the tests performed. The complete degradation of oxyfluorfen was achieved at 15°C in all cases. The best TOC removal was achieved at 30°C. In all experiments there is a residual value of TOC that may be because the formation of a reaction intermediate during microbial decomposition. This compound could be more difficult to eliminate by biodegradation. At the highest temperature, 30°C, the disappearance of low concentration pesticides solutions was faster. However, temperature inhibition problems and toxicity problems appeared when working at high concentrations.



## DETERMINATION OF CATECHINIC ANTIOXIDANTS IN TEA

J.A. Murillo, L.F. García, E. Valverde

Analytical Chemistry

Antioxidants are especially important substances in the human diet, as they are able to slow or prevent oxidizing cells in the presence of oxygen; namely, are responsible for counteracting the harmful effects of free radicals. Heimler et al.<sup>1</sup> have indicated that plant polyphenols exhibit the ability to neutralize these radicals. For example, tea leaves, which are used to prepare infusions, are natural sources of antioxidants. This communication presents an analytical method for determining the concentration of antioxidants in tea samples. The method is based on the deactivation of reactive oxygen species which are formed during the sodium perborate



decomposition, by the biophenols present in the infusion. These free radicals promote luminol oxidation, manifested by the emission of radiation in the visible region of the spectrum. However, if these biophenols, exhibiting the ability to inactivate free radicals, are in the middle, the chemiluminescent emission will decrease in proportion to the antiradical activity of such molecules.<sup>2</sup> A continuous flow system is used to carry out the proposed study. The catechinic antioxidant compounds from the tea infusions are firstly chromatographically separated and then these are guided to a chemiluminescent detector where the reaction with the mixture luminol-perborate-Co(II) takes place. The antiradical activity of different catechinic antioxidants is measured on the basis of the magnitude of the chemiluminescent inhibition signals.

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## FORMATION AND EVOLUTION OF THERMOCONVECTIVE VORTICES: APPLICATION TO ATMOSPHERIC PHENOMENA

D. Castaño, M.C. Navarro, H. Herrero

Applied Mathematics



Dust devils are columnar, ground-based whirlwinds, common in dry regions, observed in daytime and made by the dust picked up from the ground.<sup>1,2</sup> They are formed when surface isolation leads to a superadiabatic lapse rate, causing an unstable stratified atmosphere and strong convection.<sup>2,3</sup> They have a vortical structure, characterized by a spiral up motion around an eye. Dust devils frequently contain subvortices, small “parasites” or secondary circulation embedded in the primary whirl (dust devil) that normally form near the center of the dust devil and follow essentially concentric circular paths about the dust

devil center.<sup>3,4,5,6</sup> In this talk, we show that thermoconvective instability is the responsible for the formation of secondary whirls embedded in the primary axisymmetric vortex. We study the influence of the inner radius and the sharpness of the temperatura profile at the bottom on these parasitic whirls. In [3,4,5,6] it is reported the formation of subvortices embedded in dust devils that normally appear near the center of the dust devil and follow essentially concentric circular paths about the dust devil center. The base on the generation of these subvortices and their evolution is thermoconvective. Our numerical results reinforces this idea.

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## ADRENOCEPTORS SUBCELLULAR LEVELS IN WISTAR RATS: EFFECTS OF CENTRAL INFUSION OF LEPTIN AND CALORIC RESTRICTION

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Biochemistry

The hypothalamus in the Central Nervous System continuously transduces input from neural, hormonal and nutrient-related signals into responses that maintain both energy- and glucose-homeostasis. Afferent signals such as the hormone leptin convey information to the hypothalamus regarding long-term energy stores. After receiving information, the hypothalamus sends signals to peripheral organs, including the liver, to keep homeostasis. The hypothalamus signal to the peripheral organs by stimulating the autonomic nerves. Sympathetic hepatic nerves can modulate hepatocyte function by direct action of their neurotransmitter noradrenaline on  $\alpha$ - and  $\beta$ - adrenergic receptors. Alterations in connections between the brain and the liver through the adrenergic system could favor the accumulation of hepatic fat and the development of diseases such as fatty liver. In order to reveal the involvement of the autonomic nervous system in the central leptin regulation of liver function, we focus this study on neuroendocrine connections between the hypothalamus and the liver. To carry out this study, osmotic pumps were implanted, by stereotaxic surgery, in the brain of male 8-month-old Wistar rats. Animals were infused with leptin (0.2  $\mu\text{g}/\text{d}$ ) or its vehicle (PBS) for 7 days. Our results show the effects of intra-cerebroventricular leptin administration on total and sub-celullar levels of adrenergic receptors, in order to understand the ability of leptin to modulate the hepatic metabolism through Sympathetic Nervous System and shed new knowledge about anti-steatotic and anti-diabetic effects of leptin.





## STUDY OF ANTIMICROBIAL ACTIVITY OF SEVERAL YEAST SPECIES ISOLATED FROM FOOD AGAINST BACTERIAL PATHOGENS

M. Gómez, M. Fernández-González

Food Science and Technology

Chemical preservatives are commonly used to extend the life and improve the safety of food by inhibiting the growth of microorganisms. However, in response to the increasing consumers demand for so-called minimal processing food or with the least amounts of additives, it has begun to promote alternative and safety methods of food preservation, such as the use of natural antimicrobials from lactic acid bacteria or yeasts. There are very few studies of yeast antimicrobial activity against pathogenic bacteria in food and therefore, this work aims to study the inhibition of growth of five pathogenic microorganisms of food interest (*Salmonella enteritidis*, *Escherichia coli*, *Staphylococcus aureus*, *Listeria monocytogenes* and *Clostridium perfringens*) using 208 yeast strains from 15 different genera and more than 40 species isolated from food ecosystems and stored at the University of Castilla-La Mancha collection. It have been found that 90 of assayed strains showed antimicrobial activity in varying degrees against any of the pathogen tested, being *Staphylococcus aureus* and *Clostridium perfringens*, more sensitive to yeasts action unlike *Escherichia coli* and *Salmonella enteritidis*.

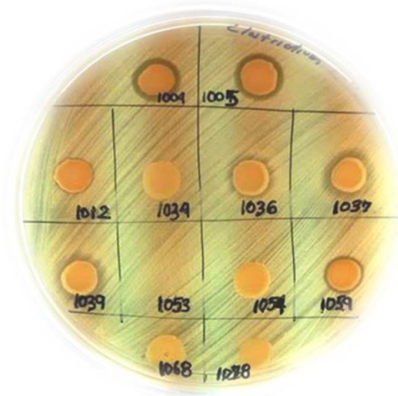


Figure 1. Inhibition of *Clostridium perfringens* by *Metschnikowia pulcherrima* y *Kluyveromyces thermotolerans*

## MORPHOLOGY SEPARATION OF VINYL-TERMINATED GOLD NANOPARTICLES (AuNPs) BY CAPILLARY ELECTROPHORESIS-DIODE ARRAY DETECTOR (CE-DAD)

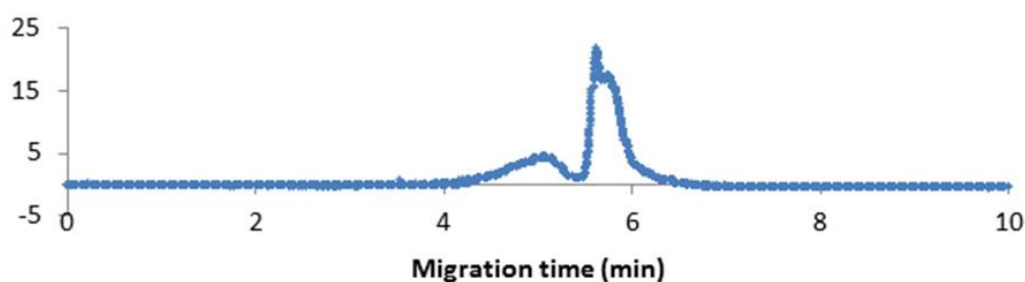
C. Adelantado, M. Zougagh, A. Ríos  
Analytic Chemistry



An easy and rapid CE-DAD methodology has been developed in order to identify and separate gold nanoparticles (AuNPs) according to their shapes –octahedra and triangles–, these AuNPs being previously synthesised and dissolved in cetyl trimethyl ammonium chloride (CTAC). A mixture of both shapes was injected into the electrophoretic system to achieve an adequate separation of them all in a mixed buffer solution of 10 mM tris(hydroxymethyl)aminomethane (Tris) and 20 mM sodium dodecyl sulfate (SDS) at pH 8.5,<sup>1</sup> and they showed maximum absorption at 200 and 580 nm wavelength when

analysed by UV-Vis spectrophotometry. Different peaks in CE-DAD were obtained for each structure (Fig. 1). A study of the influence of temperature and pH on the synthesis of the different structures of AuNPs was conducted and it was concluded that the ratio between triangles and octahedra decreased to a great extent.

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Typical electropherogram after the injection of a mixture of triangular and octahedral AuNPs (the earliest and the latest eluting, respectively).

## HELICAL CHIRAL ALUMINIUM COMPLEXES FOR THE SYNTHESIS OF CYCLIC CARBONATES AND POLYCARBONATES

M.A. Gaona, A. Lara-Sánchez, A. Otero, J.A. Castro-Osma, J. Fernández-Baeza

Inorganic Chemistry



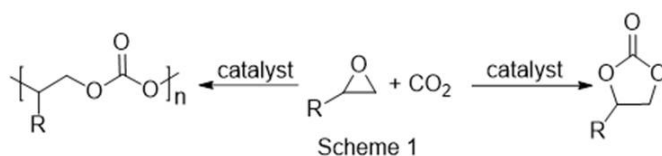
Lack of renewable carbon sources to produce energy and the increasing concentration of carbon dioxide in the atmosphere is leading into using CO<sub>2</sub> as a sustainable chemical feedstock for the chemical industry. One of the most studied reactions using carbon dioxide as a reactant is its reaction with epoxides in order to get either cyclic- or polycarbonates (Scheme 1). These reactions prove to be 100% atom-economical and they are amongst the most important commercial processes using CO<sub>2</sub> as a starting material. Both synthesis of cyclic- and polycarbonates

from carbon dioxide have been extensively investigated recently.<sup>1</sup>

Inspired by the excellent activity displayed by aluminium complexes as catalysts for these reactions,<sup>2</sup> the work described herein shows a rational development of a new family of helical chiral bimetallic and trimetallic aluminium complexes containing an acetamidate or thioacetamidate scorpionate ligand-bridge between aluminium centres and their application as catalysts for the conversion of epoxides into their corresponding cyclic carbonates and polycarbonates.

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## ANALYZING THE ETIOLOGY OF METABOLIC DISORDERS BY MEANS OF LIPIDOMIC ANALYSIS

V. López, N. Gallardo, A. Huelva

Biochemistry



Lipidomic permits to analyze the lipidome, the entire collection of chemically distinct lipid species in a cell, an organ or a biological system. For this reason Lipidomic plays an essential role in defining the biochemical mechanisms underlying lipid-related disease process through determination of alterations in cellular lipid signaling, metabolism, trafficking and homeostasis. Wistar rats like humans, increase body weight and adiposity, become hypertriglyceridemic and hyperleptinemic with aging, and our previous results point out that ageing associated alterations are responsible of this situation. Thus, we hypothesized that

these factors could be implicated in the development of insulin resistance with aging. It is well known that the hypothalamus acts sensing the level of nutrients allowing the brain to modulate energy intake and energy expenditure in order to maintain energy homeostasis. Besides body adiposity is regulated by the hormones leptin and insulin which reduce food intake while increase energy expenditure via actions on target neurons found in the hypothalamus. For all these reasons we focus our attention in this organ. This comprehensive analysis provides information about the total content and relative abundance of specific lipid species in the hypothalamus during aging, that could be correlated with the development of metabolic disorders. This information will help us to understand the mechanisms involved in the development of insulin and leptin resistance, and we will be closer to find the origin and therefore closer to get a solution.

## ELECTROCHEMICAL SYNTHESIS OF PEROXIACETIC ACID USING CONDUCTIVE DIAMOND ELECTRODES

I. Moraleda, C. Sáez, J. Llanos, M.A. Rodrigo

Chemical Engineering



Organic peroxyacids belong to a group of oxidants characterized by the presence of a peroxy group (-O-O-). One of the most important organic peroxyacids is peroxyacetic acid (PAA), which is also known as peracetic acid. PAA is used as bleaching agent and in the industrial synthesis of epoxides. The commercial PAA is supplied in equilibrium with hydrogen peroxide, acetic acid and water. Hydrogen peroxide plays a key role in PAA electrosynthesis, favoring the chemical equilibrium of PAA (according to Eq. 1) and therefore, its

stability. For this reason, the electrochemical generation of hydrogen peroxide on the cathode surface can improve the synthesis of PAA.



Recently, electrochemical oxidation with boron doped diamond (BDD) anodes have become one of the most promising technologies in the treatment of industrial waste pollutions with organics and in the electroynthesis or oxidants. BDD anodes have higher chemical and electrochemical stability, as well as higher current efficiency in the above-mentioned processes. The aim of this work is the study of the technical viability of the electrochemical synthesis of PAA with BDD anodes, optimizing the operating conditions that maximize the production of this organic peroxyacid. For this, the influence of, current density, pH, cell configuration and raw material in the PAA production rate and efficiency has been studied.

### Acknowledgements

This work has been supported by JCCM (Junta de Comunidades de Castilla-La Mancha) through the project PEII-2014-039-P.

## DECORATION OF MULTI-WALLED CARBON NANOTUBES WITH METAL NANOPARTICLES IN SUPERCRITICAL CARBON DIOXIDE: A NOVEL APPROACH FOR THE MODIFICATION OF SCREEN PRINTED ELECTRODES

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Analytical Chemistry



Functionalized multi-walled carbon nanotubes (MWCNTs) have been decorated with metal nanoparticles in supercritical dioxide medium. This approach permits the rapid and simple decoration of carbon nanotubes with the metal of choice. The prepared nanomaterials were used to modify screen-printed electrodes, improving their electrochemical properties and allowing to obtain a wide range of working electrodes based on carbon nanotubes. A mixture of acids functionalization of MWCNTs is used as a means to

facilitate the deposition of metals. These electrodes were applied to the amperometric determination of pyridoxine (Vitamin B<sub>6</sub>) in food and pharmaceutical samples. Specifically, this method was applied in food such as dietary supplements, multivitamin preparations and energy drinks. Using Ru-nanoparticles-MWCNTs as the working electrode, better results were obtained. The limit of detection was  $0.8 \times 10^{-6} \text{ mol L}^{-1}$ . These parameters represented a 3-fold increase in sensitivity compared to the use of bare MWCNTs or other carbon-based working electrode.

**Acknowledgments:** The Spanish Ministry of Economy and Competitiveness (MINECO) and JJCCC Castilla-La Mancha are gratefully acknowledged for funding this work with Grants CTQ2013-48411-P and JCCM PEIC-2014-001-P, respectively. E.J. Llorent-Martínez acknowledges the financial support from the UCLM Research Plan. The support given through an "INCRECYT" research contract to M. Zougagh is also acknowledged.



## EFFECTS OF FEBRILE SEIZURES ON ADENOSINE RECEPTORS IN NEONATES

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Health Science



Febrile seizures have been associated with the development of epilepsy but the underlying mechanism is still poorly understood. Although febrile seizures are commonly related to the brain cortex, however, studies carried out in the last two-three decades have suggested that other sub-cortical areas, such as the cerebellum, could be also involved. In that sense febrile seizures are one of the most typical convulsive disorders in the children between 3 months and 6 years corresponding to 2 weeks of life in rodents, stage at which the cerebellum is still under development.

Adenosine is a purine nucleoside, widely recognized as an endogenous modulator of neuronal excitability, which exerts potent neuroprotective and anticonvulsant actions in the brain through adenosine receptors binding. We previously showed short term modulation of A1 and A2A adenosine receptors and 5'-nucleotidase activity in cortex from rat brain following hyperthermia-induced seizures, suggesting a possible neuroprotective role of adenosine. The aim of the present work was to investigate whether both receptors and 5'-nucleotidase activity could also be modulated in the cerebellum in response to hyperthermia-induced seizures. The hyperthermia treatment was carried out, as described previously by our group, using the hair dryer model. Neonates were sacrificed 48 hours, 5 and 20 days after hyperthermia seizures and cerebellar plasma membranes were isolated. The effect of fever seizures on A1R and A2AR was studied by radioligand binding assays using [<sup>3</sup>H]DPCPX and [<sup>3</sup>H]ZM241385 as radioligands, respectively. A1Rs were significantly increased after 48 h of hyperthermia and no significant differences were observed at 5 or 20 days. However, A2ARs were affected in a biphasic manner being decreased after 48 h and increased after 5 and 20 days of hyperthermia. Changes on receptors were accompanied by affectation of 5'-nucleotidase activity. These results suggest that adenosine could exhibit a possible neuroprotective role on hyperthermia seizures also in cerebellum.

## DOMAIN DECOMPOSITION NUMERICAL METHODS APPLIED TO RAYLEIGH-BÉNARD PROBLEMS

M.R. Ferrández, F. Pla, H. Herrero

Applied Mathematics



In Rayleigh-Bénard problems, a fluid layer is heated from below and, as a consequence, a convective motion appears for large enough vertical temperature gradients.<sup>2</sup> The aim of this work is to study a non-overlapping domain decomposition method for various Rayleigh-Bénard convection problems with different heating conditions. Three cases are studied depending on the type of heating applied at the bottom boundary: uniform heating, local heating modelled by a Gaussian profile for the temperature and heating half cell described by an arctangent function. The problem is defined in a rectangular domain

which is partitioned into two or more subdomains with appropriate interface conditions. The spectral Legendre collocation method is used to discretize the problem. Two perspectives of resolution are considered, a direct algorithm<sup>3</sup> or an iterative procedure.<sup>1</sup> Great improvements are achieved with the domain decomposition techniques in condition numbers, size of the matrices, numerical errors and computing times. Gibbs phenomenon related with singularities at the boundary is avoided. The method distinguished the local heating boundary condition to properly describe the behaviour of the fluid.

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## MICROWAVE HEATING FOR THE CONVERSION OF AGRO-INDUSTRIAL WASTE INTO VALUABLE CHEMICALS AND MATERIALS

C. Lucas-Torres, A. Lorente, B. Cabañas, A. Moreno

Organic Chemistry

High demand on fossil feedstocks represents a challenge, as the search for substitutes to help keeping the world resources at an acceptable level is of great importance.<sup>1</sup> In this sense, we propose the use of waste generated from agricultural industries as a renewable source of fuels, chemicals and materials. Microwave irradiation may be applied as main sustainable technology in several processes.<sup>2</sup>

Lignocellulosic biomass contains cellulose, hemicellulose, lignin and, in the primary cell wall, pectin. The microwave treatment of the carbohydrate fraction is of special interest in the biofuel field.<sup>3</sup> Lignin is known as the most important source of antioxidant phenolics. However, this presentation will focus on the pectin, as an interesting gelling agent, and cellulose extraction from mango peel waste.

Pectin is conventionally extracted at high temperatures under acidic conditions from several fruits.<sup>4</sup> Low temperature microwave-assisted acid-free extraction of pectin allows to obtain higher yields from three different mango cultivars, comparing with the conventional conditions. Structural studies on the de-pectinated peel reveal a cellulose composition, which can be isolated. Interestingly, a second microwave treatment on these residues retained mesoporosity whilst significantly increasing surface area and pore volume,<sup>5</sup> proposing a new material with adsorbent or catalytic applications.



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## En el próximo número de Molécula...

En el número de junio incluiremos los actos de investidura de nuevos doctores "Honoris causa", el campus científico tecnológico, las jornadas de catálisis y recopilaremos las Tesis defendidas y las Conferencias impartidas en los dos últimos meses. También nuestras habituales secciones de investigación y cafetería.