

X Edición Premios José Antonio García Domínguez

En el marco de las 14^{as} Jornadas de Análisis Instrumental (XIV Reunión Científica de la Sociedad Española de Cromatografía y Técnicas Afines, SECyTA) celebradas en Barcelona del 1 al 3 de octubre de 2014 se otorgaron los premios José Antonio García Domínguez a las mejores comunicaciones orales y tipo cartel presentadas en dicha reunión. Al igual que en años anteriores, esta X edición de los premios ha sido patrocinada por Bruker. El jurado encargado de fallar los premios correspondientes a las mejores comunicaciones orales estaba formado por Jordi Díaz Ferrero (presidente), Ana M^a García Campaña, Javier Moreno Andújar y Juan V. Sancho Llopis, que tras debatir los méritos científicos de las presentaciones, tomó por unanimidad los siguientes acuerdos:

1^{er} Premio ex-aequo a la mejor Comunicación Oral (400 euros)

Comunicación: AME-OC09

Título: DEVELOPMENT OF AN ANALYTICAL METHOD FOR DECHLORANE PLUS AND RELATED COMPOUNDS IN FISH SAMPLES

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1^{er} Premio ex-aequo a la mejor Comunicación Oral (400 euros)

Comunicación: AME-OC12

Título: PART-PER-QUADRILLION DETERMINATION OF FULLERENES IN SURFACE WATERS, SOILS, AND SEDIMENTS

Autores: J.À. Sanchís⁽¹⁾, C. Bosch⁽¹⁾, L.F. Silva⁽²⁾, M. Farré⁽¹⁾, D. Barceló⁽¹⁾
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2^o Premio a la mejor Comunicación Oral (600 euros)

Comunicación: TOM-OC08

Título: HIGH RESOLUTION TANDEM MASS SPECTROMETRY AS A CHALLENGING TOOL IN BIOLOGICALLY ACTIVE COMPONENTS: BIOPROSPECTING

Autores: J. Rubert, K. Hurkova, M. Zachariasova, J. Hajslova
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En el caso de los premios a las mejores comunicaciones tipo cartel presentadas en las 14^{as} Jornadas de Análisis Instrumental (XIV Reunión Científica de la SECyTA), el jurado, constituido por Yolanda Picó (presidenta), Mercedes de Frutos, Marinela, Belén Gómara y Javier Santos, tomó por unanimidad los siguientes acuerdos:

1^{er} Premio al mejor Póster (400 euros)

Comunicación: AMA-P01

Título: IN-SYRINGE DISPERSIVE LIQUID-LIQUID MICROEXTRACTION AND SILYLATION OF UV FILTERS IN WATER SAMPLES COUPLED TO GC/MS

Autores: S. Clavijo Roa⁽¹⁾, J. Avivar Cerezo⁽²⁾, V. Cerdà Martín⁽³⁾

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2^o Premio al mejor Póster (300 euros)

Comunicación: OQA-P04

Título: FIELD-FLOW FRACTIONATION AND CAPILLARY ELECTROPHORESIS OF FUNCTIONALIZED FULLERENES

Autores: A. Astefanei⁽¹⁾, W. Kok⁽²⁾, O. Nuñez⁽¹⁾, M.T. Galceran⁽¹⁾, P. Schoenmakers⁽²⁾

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La entrega de los premios tuvo lugar el 3 de octubre de 2014, durante la ceremonia de clausura de las 14^{as} Jornadas de Análisis Instrumental (XIV Reunión Científica de la SECyTA).

Belén Gómara
Secretaria de la SECyTA

1^{er} Premio ex-aequo a la mejor Comunicación Oral (400 euros): comunicación AME-OC09

DEVELOPMENT OF AN ANALYTICAL METHOD FOR DECHLORANE PLUS AND RELATED COMPOUNDS IN FISH SAMPLES

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Dechlorane Plus (DP) is a flame retardant additive used in polymeric systems such as electrical hard plastic connectors in televisions and computer monitors, wire coatings and furniture. This product, currently classified as a high production volume chemical by the U.S. EPA, was created by OxyChem in the 70s when Mirex, another flame retardant from the same company, was banned. The existence of DP in the environment was first detected in samples from the Great Lakes in 2006. Since then, studies have been performed in order to determine the environmental behavior and presence of this compound and its main relatives: Dechlorane 602, 603 and 604. These compounds have been mainly studied in environmental matrices, such as water, air, soil and biota with monitoring purposes, but the dietary exposure to these chemicals has been hardly investigated. Thus, there is a need for the development of analytical methods for the determination of these compounds on food and feed matrices. In this work, we focus on fish samples. The main steps of the methodology are the following: (1) addition of ¹³C-labelled internal standards, (2) extraction, (3) clean-up, (4) concentration (5) instrumental determination by HRGCHRMS and (6) quantitation.

Extraction was performed in Soxhlet apparatus. Several solvents (hexane, hexane:acetone 41:59 and hexane:dichloromethane 50:50) and different extraction time (3 h, 6 h, 12 h and 24 h) were tested.

Clean up was based on the purification on a multilayer silica column. However, an additional purification in a pyrenyl HPLC column was tested. Results showed that dechlorane compounds eluted between 3.5 min and 10 min, using hexane as mobile phase at 1 ml/min. Residual interferences from the matrix were discarded in the first fraction (0 to 3.5 min).

Instrumental determination was performed with an Agilent 6890N gas chromatograph coupled to an Autospec Ultima high resolution mass spectrometer, operating in the SIR mode at 35 eV (EI) and 10,000 resolving power. Two fragments for each compound were monitored in time windows. Quantification was carried out by the isotopic dilution method, based on the use of ¹³C-anti DP. Accuracy, precision, linearity, limit of detection and limit of quantification of the method were evaluated in real samples.

1^{er} Premio ex-aequo a la mejor Comunicación Oral (400 euros): comunicación AME-OC12

**PART-PER-QUADRILLION DETERMINATION OF FULLERENES IN SURFACE
WATERS, SOILS, AND SEDIMENTS**

J.À. Sanchís ^{(1)*}, **C. Bosch** ⁽¹⁾, **L.F. Silva** ⁽²⁾, **M. Farré** ⁽¹⁾, **D. Barceló** ⁽¹⁾

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Fullerenes are carbon based nanomaterials in a hollow-spherical shape which, during the recent years, have been extensively studied from an environmental point of view. While some relevant aspects of their behaviour, fate and their ecotoxicity effects start to be well understood, their quantification in real environmental samples is still an analytical challenge, mostly because of their extremely low concentration levels of these nanomaterials. In comparison with other emerging contaminants, very few works have reported the occurrence of fullerenes in the environment. Nevertheless, characterizing their concentrations in several environmental compartments is an important task for properly assessing the real environmental risks of fullerenes.

In this work, several types of environmental matrices (river water, wastewater, soils and sediments) have been analyzed by liquid chromatography (LC), with buckyprep columns, coupled with an atmospheric photoionization source (APPI) to a high resolution mass spectrometer (HRMS) with a hybrid quadrupole-orbitrap analyzer. This instrumentation offers unique sensitivity and selectivity and the method performance allows the detection of fullerenes in the low pg/L order in water samples. The performance of the method will be comprehensively compared with other previous methods based in electrospray ionization (ESI) and C18 based LC.

Surface water and sediments samples from two rivers from Barcelona (Spain), under high anthropogenic pressure, have been analyzed, showing concentrations of fullerenes in the pg/L order. Results about their occurrence of fullerenes, their aggregation, heteroaggregation and partition to the sediments will be exposed. In addition, the analysis of soils from Sul Catarinense (Brazil) will be presented. Fullerenes C60 and C70 were detected at pg/g concentrations in those samples which were located close to the largest fossil combustion power station in Latin America. Urban samples also exhibited significant levels of fullerenes while rural soils levels were under the limit of detection in about 50% of the samples.

Acknowledgements: This work has been supported by the Spanish Ministry of Science and Innovation through the project Nano-Trojan (CTM-2011-24051).

2º Premio a la mejor Comunicación Oral (600 euros): comunicación TOM-OC08

HIGH RESOLUTION TANDEM MASS SPECTROMETRY AS A CHALLENGING TOOL IN BIOLOGICALLY ACTIVE COMPONENTS: BIOPROSPECTING

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During the last decade, consumers' interest to support their health through the use dietary supplements or nutraceuticals continues to increase. In this context, searching for new sources of biologically active substances with positive health effects realizes a great challenge. For example, the deep waters surrounding the coastline of the sea represent an exciting biotope for marine exploration. Dark and cold Arctic water generates a hostile environment where the ability to adapt is crucial to survival. These waters are nonetheless bountiful and a diverse plethora of marine organisms thrive in these extreme conditions, many with the help of specialized chemical compounds. This presentation will demonstrate a comprehensive analytical strategy we have already used in investigation of bio-matrixes for which the composition is completely unknown. The following steps were taken and critically evaluated: (i) various ways of mechanical treatment of algae biomass to disintegrate the cell walls and increase the extraction efficiency, (ii) extraction-fractionation steps enabling isolation of polar, medium-polar, and non-polar compounds, and selection of the optimal approach (iii) evaluation for non-target screening of fingerprinting followed by assessment of different forms of identified compounds employing ultraperformance liquid chromatography coupled with high resolution tandem mass (HRMS/MS). For example, fish skins, which are commonly waste material, were evaluated and potential bioactives components were found, such as Gadusol, its ability to reduce radicals is comparable to that of ascorbic acid.

Subsequently, mammalian cell may be used to carry out a broad metabolomics studies. UHPLCHRMS could obtain a global metabolomic examination of the effect of a food extract (fraction) or bioactive component in different mammalian cells, in this case human breast cancer and prostate cancer cells were evaluated for algae extracts and sesquiterpene lactones (trilobolide extracts), respectively. In this way, changes in the metabolome, intracellular and extracellular metabolites, were explored using liquid chromatography coupled to high resolution tandem mass spectrometry (UHPLC-Triple TOF 5600 (AB Sciex)). Consecutively, data analysis was carried out using various chemometric tools, such as Marker View (AB Sciex) and SIMCA (Umetrics). The identification of markers showed different cell responses, metabolite pathways, to different treatments.

1^{er} Premio al mejor Póster (400 euros): comunicación AMA-P01

IN-SYRINGE DISPERSIVE LIQUID-LIQUID MICROEXTRACTION AND SILYLATION OF UV FILTERS IN WATER SAMPLES COUPLED TO GC/MS

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A fully automated method for the determination of seven ultraviolet (UV) filters, commonly included in the formulation of sunscreen products, in aqueous samples is presented. The proposed method is based on the use of the in syringe dispersive liquid–liquid microextraction (DLLME) technique, coupled as front end to gas chromatography - mass spectrometry (GC–MS). This method enabled the integration of the extraction steps, derivatization and sample injection in an instrumental setup easy to operate. Derivatization with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) was used to increase the volatility of hydroxylated analytes and to improve sensitivity. Although BSTFA is prone to hydrolysis in presence of water and is therefore unstable in aqueous solutions, it was compatible with the DLLME process due to the kinetics of the derivatization and given that extraction of the hydroxylated UV filters is faster than the decomposition of BSTFA.

Dispersion was achieved by aspiration of the organic (extractant and disperser) and the aqueous phase into the syringe very rapidly. The denser-than-water organic droplets released in the extraction step, were accumulated at the head of the syringe, where the sedimented fraction was transferred to a loop where the ultrasonication and derivatization take place. After silylation the sedimented phase was transported to a micro-volume injection valve where finally was introduced via an air stream into the injector of the GC, through a stainless steel tubing used as interface. Factors affecting the microextraction efficiency were optimized using multivariate optimization.

Acknowledgements: This work was funded by the Government of the Balearic Islands (43/2011 co-financed by FEDER funds) and the Spanish Ministry of Science and Innovation (MICINN) through the project CTQ2010-15541.

2º Premio al mejor Póster (300 euros): comunicación OQA-P04

FIELD-FLOW FRACTIONATION AND CAPILLARY ELECTROPHORESIS OF FUNCTIONALIZED FULLERENES

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Fullerenes are carbon-cage nanoparticles with widespread commercial and industrial application. Nowadays, fullerenes functionalized with polar groups are produced in high quantities, especially for use in pharmaceutical and clinical applications (e.g. as drug carriers, tumor inhibitors). Fullerenes are increasingly studied in relation to their potential risk for the environment and human health. However, they show a strong tendency to aggregate into clusters, which alters their reactivity, toxicity, fate and transport in the environment. In this context, it is important to develop specific analytical methods for (functionalized) fullerenes and especially for their aggregates. In this study asymmetrical flow field-flow fractionation (AF4) and capillary electrophoresis (CE) are used to fractionate and characterize functionalized fullerene aggregates.

AF4 is a versatile technique that allows the separation and characterization of aggregates over a wide size range, from nano- to micrometers. Till now, AF4 has been used mostly for the characterization of pristine fullerene aggregates in water (aqu/C60) [1]. Another technique that can be used for the physicochemical characterization and separation of species from low molecular weight (inorganic ions) to complex organic molecules (proteins, nucleic acid, peptides, etc) is capillary electrophoresis (CE) and its application to the analysis of fullerene compounds has been previously reported [2]. In this work, AF4 with multi-angle light scattering (MALS) detection and CE-UV were used to study the aggregation behavior of functionalized fullerenes (polyhydroxyfullerenes and carboxylic C60-derivatives). The AF4-MALS results showed that the retention of the fullerenes increased with the ion strength due to a decrease of the electrostatic repulsion between the channel wall and the fullerenes. Polyhydroxyfullerenes showed small particle sizes (≈ 10 nm) with increasing aggregation with the ionic strength. In contrast, the size of the carboxylic C60-derivative aggregates was significantly larger (≈ 300 nm) in pure water, but decreased with the addition of salt, possibly due to the higher hydrophobicity of these compounds compared with polyhydroxyfullerenes. The electrophoretic behavior of functionalized fullerenes was studied at different pH values and ionic strengths. The ionic strength affected significantly the shape of the electrophoretic peaks due to a change in the size of the aggregates, as was also demonstrated by the AF4-MALS results.

[1] Isaacson, C.W.; Bouchard, D. *J. Chromatogr. A* 1217 (2010) 1506-1512.

[2] Astefanei, A.; Nuñez, O.; Galceran, M.T. *Anal Bioanal. Chem.* 404 (2) (2012) 307-13.