

XV Edición Premios José Antonio García Domínguez

En el marco de la XIX Reunión Científica de la Sociedad Española de Cromatografía y Técnicas Afines (SECyTA) celebrada en Santiago de Compostela del 8 al 11 de octubre de 2019 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 XV 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 Joan Grimalt Obrador (presidente), Jordi Díaz Ferrero, Belén Gómara Moreno y Begoña Jiménez, que tras debatir los méritos científicos de las presentaciones, tomó por unanimidad los siguientes acuerdos:

1^{er} Premio a la mejor Comunicación Oral (800 euros)

Comunicación: OY-20

Título: POTENTIAL OF MICRO-LIQUID CHROMATOGRAPHY FOR THE DETERMINATION OF PSYCHOACTIVE SUBSTANCES IN WASTEWATER

Autores: Alberto Celma ^{1*}, Juan V. Sancho ¹, Noelia Salgueiro-González ², Sara Castiglioni ², Ettore Zuccato ², Félix Hernández ¹, Lubertus Bijlsma ¹

¹ *Research Institute for Pesticides and Water, University Jaume I, E-12071 Castelló, Spain.*

² *Istituto di Ricerche Farmacologiche Mario Negri - IRCCS, Dep. of Environmental Health Science, I-20156 Milan, Italy*

2^o Premio a la mejor Comunicación Oral (600 euros)

Comunicación: OY-19

Título: ATMOSPHERIC PRESSURE PHOTOIONIZATION FOR GC-HRMS ANALYSIS OF PCDD/Fs AND DIOXIN-LIKE PCBs IN FOOD AND ENVIRONMENTAL SAMPLES

Autores: J. F. Ayala-Cabrera ^{1*}, M. Ábalos ², E. Abad ², E. Moyano ¹, F. J. Santos ¹

¹ *Department of Chemical Engineering and Analytical Chemistry, University of Barcelona, E-08028 Barcelona, Spain*

² *Laboratory of Dioxins, Institute of Environmental Assessment and Water Research (IDAEA-CSIC), E-08034 Barcelona, Spain*

En el caso de los premios a las mejores comunicaciones tipo cartel presentadas en la XIX Reunión Científica de la SECyTA, el jurado, constituido por Fco. Javier Santos Vicente (presidente), Juan Vicente Sancho Llopis, José A, González Pérez, Núria Fontanals Torroja y Ana Maria García Campaña, tomó por unanimidad los siguientes acuerdos:

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

Comunicación: P-104

Título: A NOVEL METHOD TO DETERMINE FIPRONIL AND FIPRONIL SULFONE IN EGGS BY CAPILLARY ELECTROPHORESIS AND SALTING-OUT ASSISTED LIQUID-LIQUID EXTRACTION

Autores: M. Mar Aparicio-Muriana^{(1)*}, Ivona Lhotská⁽²⁾, Francisco J. Lara⁽¹⁾ and Ana M. García-Campaña⁽¹⁾

⁽¹⁾ Department of Analytical Chemistry, Faculty of Sciences, University of Granada, Av. Fuente Nueva s/n, E-18071, Granada, Spain

⁽²⁾ Charles University, Faculty of Pharmacy in Hradec Králové, Prague, Czech Republic

2^o Premio al mejor Póster (300 euros)

Comunicación: P-69

Título: STUDY OF THE PHOTODEGRADATION OF PBDES IN WATER BY UV-LED TECHNOLOGY

Autores: Meritxell Valentí ^{1*}, Rafael González-Olmos ², Jordi Díaz-Ferrero ¹

¹ Environmental Laboratory ²Chemical Engineering Department, IQS, Ramon Llull Univeristy, Via Augusta 390, 08017 Barcelona, Spain

La entrega de los premios tuvo lugar el 11 de octubre de 2019, durante la ceremonia de clausura de la XIX Reunión Científica de la SECyTA.

Juan Vicente Sancho
Secretario de la SECyTA

**POTENTIAL OF MICRO-LIQUID CHROMATOGRAPHY FOR THE DETERMINATION OF
PSYCHOACTIVE SUBSTANCES IN WASTEWATER**

Alberto Celma ^{1*}, Juan V. Sancho ¹, Noelia Salgueiro-González ², Sara Castiglioni ², Ettore Zuccato ²,
Félix Hernández ¹, Lubertus Bijlsma ¹

¹ *Research Institute for Pesticides and Water, University Jaume I, E-12071 Castelló, Spain.*

² *Istituto di Ricerche Farmacologiche Mario Negri - IRCCS, Dep. of Environmental Health Science, I-20156 Milan, Italy.*

* alberto.celma@uji.es

Wastewater-based epidemiology (WBE) can give valuable information on the extent and actual use of new psychoactive substances (NPS) and illicit drugs. Solid-phase extraction followed by UHPLC-MS/MS is normally used for the determination of both illicit drugs and NPS in wastewater. However, recently developed micro liquid chromatographic techniques (μ LC) remained unexplored in this field. The reduced flow rate used in μ LC techniques not only enhances the chromatographic performance because of the higher ionization efficiency, but it also reduces the amount of organic solvents required for the analysis moving μ LC a step forward into a greener analytical chemistry. In this study, a detailed comparison of μ LC and UHPLC, both coupled to tandem mass spectrometry, in terms of sensitivity and reproducibility has been made in the application field of WBE. As expected, a significant increase was observed for sensitivity when comparing mass normalized data (average 14-fold). Also, the overall method performance resulted in an average increase sensitivity factor of 4.5 for μ LC-MS/MS. This is of particular interest for this type of analysis where the presence of NPS and illicit drugs is usually at very low concentrations. However, large deviations in retention time (up to 0.4 min) affected the reproducibility and robustness of the methodology when it was applied to wastewater analysis. Since many of the NPS do not have its isotopically labelled standard, the utilization of retention time as an identification parameter in this study becomes essential. Therefore, further developments need to be accomplished in order to achieve a retention time reproducibility enough to validate the methodology. Although in this work μ LC-MS/MS was strongly influenced by the amount of matrix loaded in the separation device, its enhanced sensitivity and promotion of green chemistry (faster analysis time and less solvent consumption) allow to expect improved future applications, especially when analytes are present at very low concentrations.

Acknowledgement Alberto Celma acknowledges the Ministry of Economy and Competitiveness of Spain for his predoctoral grant (BES-2016-076914).

**ATMOSPHERIC PRESSURE PHOTOIONIZATION FOR GC-HRMS ANALYSIS OF PCDD/Fs AND
DIOXIN-LIKE PCBs IN FOOD AND ENVIRONMENTAL SAMPLES**

J. F. Ayala-Cabrera ^{1*}, M. Ábalos ², E. Abad ², E. Moyano ¹, F. J. Santos ¹

¹ *Department of Chemical Engineering and Analytical Chemistry, University of Barcelona, E-08028 Barcelona, Spain*

² *Laboratory of Dioxins, Institute of Environmental Assessment and Water Research (IDAEA-CSIC), E-08034 Barcelona, Spain*

* j.ayala@ub.edu

Polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and *dioxin-like* polychlorinated biphenyls (dl-PCBs) involve a wide group organic pollutants of great concern due to their high toxicity and persistence in the environment. Although in the last decades their emissions have been reduced significantly due to the application of stricter environmental regulations [1], their presence in the environment continues to be the subject of large-scale monitoring programs to guarantee the health of human being and living organisms. Currently, gas chromatography coupled to high-resolution mass spectrometry is the technique of choice for the determination of the target compounds because it provides the required sensitivity and selectivity [2], assuring the quality of the results [3]. Recently, the use of the atmospheric pressure chemical ionization (APCI) in the GC-MS determination of environmental pollutants has shown to be a promising alternative to classical ionization techniques, but information about the real capability of the atmospheric pressure photoionization (APPI) is still limited.

In this work, a GC-APPI-HRMS (Orbitrap) method has been developed for the determination of PCDD/Fs and dl-PCBs in food and environmental samples. For this purpose, the APPI operating conditions and the use of different dopants were evaluated achieving the best results in the negative-ion mode using benzene for PCDD/Fs and diethyl ether for dl-PCBs. The developed method has been validated using certified reference materials and selected samples containing a wide range of concentration levels. The results have been compared with the reference GC-HRMS method demonstrating the good performance of the GC-APPI-HRMS method.

Acknowledgement Financial support received from projects PGC2018-095013-B-I00 and 2018-SGR-310. J. F. Ayala-Cabrera thanks Spanish Ministry of Education, Culture and Sports for the PhD FPU fellowship.

References

- [1] M. Van den Berg, L.S. Birnbaum, *et al.*, *Toxicol. Sci.* 93, 223 (2006).
- [2] K.L. Organtini, L. Haimovici, *et al.*, *Anal. Chem.* 87, 7902 (2015).
- [3] E. Reiner, *J. Mass Spectrom. Rev.* 29, 526 (2009).

1^{er} Premio al mejor Póster (400 euros): comunicación P-104

**A NOVEL METHOD TO DETERMINE FIPRONIL AND FIPRONIL SULFONE IN EGGS BY
CAPILLARY ELECTROPHORESIS AND SALTING-OUT ASSISTED LIQUID-LIQUID EXTRACTION**

M. Mar Aparicio-Muriana^{(1)*}, Ivona Lhotská⁽²⁾, Francisco J. Lara⁽¹⁾ and Ana M. García-Campaña⁽¹⁾

⁽¹⁾ *Department of Analytical Chemistry, Faculty of Sciences, University of Granada, Av. Fuente Nueva s/n, E-18071, Granada, Spain*

⁽²⁾ *Charles University, Faculty of Pharmacy in Hradec Králové, Prague, Czech Republic*

* mmarapario@ugr.es

Fipronil is an insecticide that has been prohibited in food-producing animals. However, in 2017, it was involved in a European health alert due to its presence in fresh hen eggs because of an illegal use as a veterinary treatment. EU has set maximum residue limits in eggs as the sum of fipronil and its main metabolite, fipronil sulfone ($5 \mu\text{g}\cdot\text{kg}^{-1}$), so it is crucial to monitor them in these matrixes. Previous methods were restricted to liquid and gas chromatography. In the present study, we have developed the first methodology for the separation of fipronil and two metabolites, fipronil-sulfide and fipronil-sulfone by capillary electrophoresis (CE) with UV-detection. Different electrophoretic modes were evaluated. Micellar electrokinetic chromatography (MEKC) was eventually selected, using as background electrolyte a solution of 50 mM ammonium perfluorooctanoate pH 9.0 with 10% (v/v) methanol. The proposed method was combined with a simple sample treatment based on salting-out assisted liquid-liquid extraction (SALLE). Acetonitrile and ammonium sulfate were the extraction solvent and the salt selected for the determination of these compounds in eggs. However, an endogenous interferent peak did not allow fipronil-sulfide quantification using this extraction procedure but it was not a problem in the case of fipronil and fipronil sulfone. Validation parameters were investigated yielding satisfactory results. Precision, expressed as relative standard deviation, was below 14% and recoveries ranged from 83 to 88%. Limits of detection were $90 \mu\text{g}\cdot\text{kg}^{-1}$ for fipronil and $150 \mu\text{g}\cdot\text{kg}^{-1}$ for fipronil-sulfone. In terms of sensitivity, when intended for regulatory purposes, a sample treatment allowing extra preconcentration or more sensitive detectors, such as mass spectrometry (MS), would be needed in further works.

Acknowledgement This work has been sponsored by Spanish Ministry of Economy and Competitiveness (Project ref: AGL2015-70708-R) and EU Funds. MMAM is grateful for a predoctoral grant from The Ministry of Science, Innovation and Universities (FPU17/03810). FJL is grateful for personal funding through the Special Research Program of the University of Granada.

2º Premio al mejor Póster (300 euros): comunicación P-69

STUDY OF THE PHOTODEGRADATION OF PBDES IN WATER BY UV-LED TECHNOLOGY

Meritxell Valentí ^{1*}, Rafael González-Olmos ², Jordi Díaz-Ferrero ¹

¹*Environmental Laboratory* ²*Chemical Engineering Department*

IQS, Ramon Llull University, Via Augusta 390, 08017 Barcelona, Spain.

*meritxellvalentiq@iqs.edu

Polybrominated diphenyl ethers (PBDEs) have been one of the most employed family of flame retardants and are considered as persistent organic pollutants. For that reason, this project assesses the photodegradation of PBDEs in water samples applying advanced oxidation processes (AOPs). The combination of AOPs and UV-LED radiation can be an effective treatment against a wide range of macropollutants, microorganisms and micropollutants such as phenols, pesticides or pharmaceuticals. To study the photodegradation of PBDEs in water samples, irradiation was applied using the PearlBeam T255/265/285 device, which provides three different wavelengths: 255 nm, 265 nm and 285 nm. First set of experiments were performed with spiked purified water samples in order to determine the best degradation conditions (wavelength, time). Then, the optimized methodology was applied to real water samples from different sources: superficial continental, marine, influent and effluent samples from two different wastewater treatment plants and a greywater sample.

For the analyses of both spiked and real samples, three consecutive LLE extractions of the samples were performed with hexane and followed by two purification columns: an anhydrous sulphate column and an acidic silica column. Extracts were concentrated to 25 µl and the analyses were performed by GC-HRMS. Best PBDE degradation results studied in spiked samples were achieved after irradiating samples at 285 nm during 240 min, reaching degradations from 50 to 87 % for all the congeners. Moreover, results of the repeatability studies pointed out that main contribution of the whole process variability came from the irradiation step (18 % < RSD < 50 %) in comparison to the analytical contribution (3 % < RSD < 10%). Real water samples were spiked and exposed to 4 hours of irradiation at 285 nm. Successful photodegradation of PBDEs ranging 51 % to 97 % was achieved for all the PBDE congeners in the different water samples with the exception of the coastal one, in which only a 31 % of degradation was achieved.

Acknowledgement The authors gratefully acknowledge the financial support of Secretari d'Universitats i Recerca del Dept. d'Empresa i Universitats de la Generalitat de Catalunya (REULED project, 2018-URL-PROJ-051).