## XII Edición Premios José Antonio García Domínguez

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En el marco de la XVI Reunión Científica de la Sociedad Española de Cromatografía y Técnicas Afines (SECyTA) celebrada en Sevilla del 2 al 4 de noviembre de 2016 se otorgaron los premios José Antonio García Domínguez a las mejores comunicaciones orales y tipo cartel presentadas en dicha reunión. Como en anteriores ediciones, esta XII edición de los premios ha sido patrocinada por Bruker.

**1er Premio a la mejor Comunicación Oral (800 euros)**

Comunicación: OJ-ENV-2

Título: UHPLC-API-MS/MS vs GC-MS for the determination of semivolatile fluorinated organic compounds

Autores: Juan Francisco Ayala Cabrera, Francisco Javier Santos Vicente, Encarnación Moyano Morcillo.

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

Comunicación: OJ-CPA-2

Título: Coupling Micellar Electrokinetic Chromatography with Mass Spectrometry Using a Volatile Surfactant for the Therapeutic Monitoring of Benzimidazoles in Animal Urine

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**1er Premio al mejor Póster (400 euros)**

Comunicación: P-CPA-11

Título: High Resolution Mass Spectrometry For The Identification Of In-Vivo 5-Meo-Mipt Metabolites In Mouse Serum And Urine

Autores: D. Fabregat-Safont[(1)], M. Ibáñez[(1)], F. Martínez García[(2)], C. Agustín-Pavón[(2)], A. Martín-Sánchez[(2)], J.V. Sancho[(1)], F. Hernández[(1)]

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**2º Premio al mejor Póster (300 euros)**

Comunicación: P-FA-36

Título: Nanoflow Liquid Chromatography High Resolution Mass Spectrometry for Multi-Residue Analysis of Veterinary Drugs in Food Samples of Animal Origin

Autores: J. Alcántara-Durán, David Moreno-González, Antonio Molina-Díaz, Juan F. García-Reyes

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La entrega de los premios tuvo lugar el día 4 de noviembre de 2016 durante la ceremonia de clausura de la XVI Reunión Científica de la SECyTA.

**Juan Vicente Sancho**
**Secretario de la SECyTA**

**1er Premio a la mejor Comunicación Oral (800 euros): Comunicación OJ-ENV-2**

# UHPLC-API-MS/MS vs GC-MS FOR THE DETERMINATION OF SEMIVOLATILE FLUORINATED ORGANIC COMPOUNDS

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Fluorotelomer olefins (FTOs), fluorotelomer alcohols (FTOHs), perfluorinated sulfonamides (FOSAs) and perfluorinated sulfonamide ethanol (FOSEs) are semivolatile fluorinated organic compounds partially or totally saturated by fluorine atoms. The study about FTOHs, FOSAs and FOSEs has been increased in the last years as a consequence of their distribution and mobility in the environment and their capability to be degraded into the persistent organic pollutant PFOA and PFOS [1]. However, there are few works reported about FTOs although it has been suggested their degradation to perfluorinated carboxylic acids (PFCAs) [2].

The non-ionic fluorinated compounds can be analyzed by GC-MS but some of them show retention and sensitivity problems due to the high volatility and ionization efficiency. In this work, we evaluate different strategies to improve both the chromatographic and ionization behavior of these compounds for their simultaneous determination by both GC-MS and UHPLC-MS.

The chromatographic separation of fluorinated compounds has been studied using different GC capillary columns. The low retention of some of them made necessary the careful selection of the sample solvent to avoid the peak overlapping. For instance, methanol, dichloromethane or methyl tert-buthyl ether have been tested and methanol provided the best performance for all the compounds. The ionization behavior has also been studied using classical ionization techniques (EI, PCI and NICI) and the best performance was obtained when using EI as ionization source. Nevertheless, difficulties observed that may hinder the detectability by GC-MS are discussed in this work.

As alternative to the GC-MS determination, LC-MS was evaluated using APCI and APPI as ionization source for the analysis of the whole families of compounds. The effect of mobile phase composition (solvent and additives) on the response has been studied and the results indicated that APPI source showed the best sensitivity for FTOHs, FOSAs and FOSEs employing acetonitrile as organic solvent and a toluene post-column addition as dopant. Nevertheless, APCI showed the best sensitivity for FTOs, employing acetonitrile as organic modifier. Considering these results, chromatographic separation was optimized to provide a sensitive and selective LC-MS method as alternative to the GCMS ones. Both UHPLC-MS/MS and GC-MS methods were validated and evaluated their applicability to the determination of semivolatile fluorinated organic compounds in water and consumer products.

[1] H. Fromme, S. Tittlemier, W. Völkel, M Wilhelm, D. Tardella, *Int. J. Hyg. Environ. Health* **213** (2009) 239-270.
[2] K. Prevedouros, I. T. Cousins, R. C. Buck, S. H. Korzeniowski, *Environ. Sci. Technol*. **40** (2006) 32-44.

**2º Premio a la mejor Comunicación Oral (600 euros): Comunicación OJ-CPA-2**

# COUPLING MICELLAR ELECTROKINETIC CHROMATOGRAPHY WITH MASS SPECTROMETRY USING A VOLATILE SURFACTANT FOR THE THERAPEUTIC MONITORING OF BENZIMIDAZOLES IN ANIMAL URINE

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Therapeutic drugs monitoring in veterinary medicine is a useful tool to assess when an animal has attained therapeutic concentration of a particular drug depending on the administered dose [1]. This can be the case of benzimidazoles (BZs), which are anthelmintic agents widely used in the prevention and treatment of parasitic infections in livestock [2] but excessive concentrations of BZs in animal biological fluids can lead to congenic malformations, teratogenicity and pulmonary edemas [3]. In this work a novel method based on micellar electrokinetic chromatography-tandem mass spectrometry (MEKC-MS/MS) has been proposed and validated for the identification and simultaneous quantification of thirteen BZs in animal urine samples (sheep, cow and goat). Separation was performed in a bare fused-silica capillary (1 m total length, 50 µm i.d). The electrophoretic separation was achieved using a voltage of 25 kV and a temperature of 25 ˚C. The running buffer was an aqueous solution of 50 mM perfluorooctanic acid adjusted to pH 9.0 with ammonium hydroxide. Direct coupling of MEKC to MS is possible using because the perfluorooctanic acid used in the separation buffer is a volatile surfactant. The sample was hydrodynamically injected for 75 s at 50 mbar and the sample solvent was water, allowing an on-line preconcentration based on sweeping of the analytes. The coaxial sheath-liquid sprayer used for CE-MS coupling consisted of ethanol/water/formic acid (50:49.5:0.5,v/v/v) and was delivered at a flow rate of 1.7 mL min-1 by syringe pump. The ESI voltage was set to -4500 V (positive mode). Other electrospray parameters at optimum conditions were: nebulizer pressure, 6 psi; dry gas flow rate, 8 L min-1; and dry gas temperature, 250 ˚C. An ion trap analyzer operating in the multiple reaction monitoring mode (MRM) was used for detection.

Under optimum conditions, sensitivity enhancement factors ranged from 50 to 181 for the studied compounds. The applicability of the proposed method was demonstrated by the determination of BZs in animal urine samples employing as sample treatment just a 1:10 dilution with water. Good linearity was obtained (R2> 0.993) for all BZs. Recoveries for fortified samples were higher than 82.3 %, with RSDs lower than 7.6 %. The limits of detection were below 69.3 µg L-1. The main advantages of the proposed method are the simplicity of operation, the rapidity to achieve a very high sample throughput with low cost and reduced waste. This method can help veterinarians to customize the administered dose of BZs for each individual case.

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[1] A. Loyacano, J. Williams, J. Gurie and A. DeRosa, Vet. Parasitol. 107, (2002), 227-234
[2] M. Danaher, H. De Ruyck, S.R.H. Crooks, G. Dowling, M. O'Keeffe, J. Chromatogr. B , 845 (2007) 1-37.
[3] B. Kinsella, S.J. Lehotay, K. Mastovska, A.R. Lightfield, A. Furey, M. Danaher, Anal. Chim. Acta. 637, (2009) 196–207.

**1er Premio al mejor Póster (400 euros): Comunicación P-CPA-11**

# HIGH RESOLUTION MASS SPECTROMETRY FOR THE IDENTIFICATION OF IN-VIVO 5-MEO-MIPT METABOLITES IN MOUSE SERUM AND URINE

**D. Fabregat-Safont[(1)], M. Ibáñez[(1)], F. Martínez García[(2)], C. Agustín-Pavón[(2)], A. Martín-Sánchez[(2)], J.V. Sancho[(1)], F. Hernández[(1)]**

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The consumption of new psychoactive substances (NPS) has increased in the last years. New compounds are being continuously detected and identified in seizures and products sold on the Internet. There is therefore an increasing need of procedures to evaluate not only the identity of the NPS present in the legal highs but also their consumption. These procedures are commonly based on the detection of markers related with a specific compound, usually its metabolites, in biological fluids. High resolution mass spectrometry (HRMS) has proved to be a powerful technique for metabolite structure elucidation. This technique in combination with metabolism studies, such as in-vivo experiments, would allow obtaining consumption biomarkers for investigating drug use or intoxications.

In this work, metabolism of the tryptamine 5-MeOMiPT was studied using liquid chromatography coupled to quadrupole-time of flight mass spectrometry (LC-QTOF MS) using adult male mice of the inbred strain C57BLJ/6. This allowed obtaining Phase I and Phase II metabolites in different biological fluids, such as urine and serum, and evaluating the metabolism of this compound over time. Thus, 16 µg of 5-MeO-MiPT (being in the range of a typical dose of 0.27 mg/kg) were injected i.p. to the mouse specimens, using NaCl 0.9% and 1% DMSO solution as drug carrier. Four groups of three specimens each were injected with the drug solution (150 µL), while one additional group of four specimens was injected with the drug carrier solution and used as control group.

Urine samples were collected at 60 min for one of the groups injected with the drug and for the control group. Urine samples were directly injected into the LC-QTOF MS system after simple dilution and also after hydrolysis with β-glucuronidase. Regarding serum samples, they were collected at 10, 20, 40 and 60 min for the drug groups, and at 60 min for the control group. Serum samples were injected after protein precipitation with acetonitrile, evaporation of organic solvent and reconstitution with the mobile phase.

The resulting metabolites were detected and tentatively identified making use of the accurate-mass information provided by QTOF MS for both (de)protonated molecule and fragment ions, after comparing control and positive samples. Additionally, the common fragment pathway and mass defect filter strategies were also evaluated.

**2º Premio al mejor Póster (300 euros): Comunicación P-FA-36**

## NANOFLOW LIQUID CHROMATOGRAPHY HIGH RESOLUTION MASS SPECTROMETRY FOR MULTI-RESIDUE ANALYSIS OF VETERINARY DRUGS IN FOOD SAMPLES OF ANIMAL ORIGIN

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The presence of veterinary drugs residues in the food chain is of increasing concern provided the adverse effect for human health, such as allergic reactions and the possible development of antibiotic bacterial resistance. For this reason, the European Union (EU) has established a maximum residue limit (MRL) for some antibiotics in foods from animal origin. Downsizing the flow stream in liquid chromatography electrospray tandem MS has been proven to be an interesting alternative to standard analytical size approaches, provided the significant benefits in terms of sensitivity and matrix effect reduction. In this sense, the use of nanoflow liquid chromatography coupled to nanospray MS detection has been restricted so far to selected bioanalytical applications (eg. proteomics). The introduction of more robust and reproducible ultra-high pressure nanoflow LC instrumentation along with new column technology integrating the nanospray spray emitter and the column in a single item, has made accessible such sophisticated approach to routine work, avoiding typical nanoflow operation issues. In this work, a nanoflow LC-MS method has been developed for the multiresidue determination of veterinary drugs in different food matrices. A Thermo Scientific EASY-nLC 1000 nano-LC system was used. An EASY-Spray column (PepMap®, C18, 3 µm, 100Å, 75 µm x 150 mm) was employed. Mobile phases A and B were water and acetonitrile, respectively, both with 0.1 % formic acid. The injection volume was 1 µL. Flow rate was set at 300 nL·min-1. A Thermo Q-Exactive Orbitrap mass spectrometer equipped with an Easy-Spray nano-electrospray ion source was used. Q-Exactive was operated in all ion fragmentation and full scan modes. The proposed method was applied to the determination of veterinary drugs in food samples such as milk, honey, egg and beef. Salting-out supported liquid extraction was selected as sample treatment. From the results obtained, the sensitivity achieved with this configuration enables the implementation of high dilution factors (1:50) in veterinary drug residue workflows without compromising sensitivity and yet, performing limit of quantitation (LOQ) between 0.03 to 3000 ng Kg-1. These LOQs were significantly lower than their corresponding MRL set. The precision was also evaluated, obtaining RSD values lower than 20% in all cases.