XIII Edición Premios José Antonio García Domínguez

En el marco de la XVII Reunión Científica de la Sociedad Española de Cromatografía y Técnicas Afines (SECyTA) celebrada en Barcelona del 3 al 5 de octubre de 2017 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 XIII 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 Juan Vicente Sancho (presidente), Jordi Díaz Ferrero, Ana Mª García Campaña y Marta Lores Aguín, que tras debatir los méritos científicos de las presentaciones, tomó por unanimidad los siguientes acuerdos:

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

Comunicación: O-YS-08

Título: ION MOBILITY MASS SPECTROMETRY AS A NOVEL TOOL FOR SUPPORTING STEROIDOMICS STUDIES

Autores: Maykel Hernández-Mesa, Antoine Escourrou, Fabrice Monteau, Gaud Dervilly-Pinel, Bruno Le Bizec

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

Comunicación: O-YS-05

Título: USE OF NANOFLOW LIQUID CHROMATOGRAPHY HIGH RESOLUTION MASS SPECTROMETRY FOR THE DETERMINATION OF PESTICIDES IN SPECIFIC PART OF BEES, POLLEN AND NECTAR

Autores: David Moreno-González [(1)], Jaime Alcántara-Durán [(1)], Juan F. García-Reyes [(1)], Antonio Molina-Díaz [(1)], Victor Cutillas [(2)], Amadeo R. Fernández-Alba [(2)]

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En el caso de los premios a las mejores comunicaciones tipo cartel presentadas en la XVII Reunión Científica de la SECyTA, el jurado, constituido por Fco. Javier Santos Vicente (presidente), Francisco Javier Moreno, Núria Fontanals, Belén Gómara Moreno y Begoña Jiménez Luque, tomó por unanimidad los siguientes acuerdos:

1er Premio al mejor Póster (400 euros)

Comunicación: P-29

Título: FAST CHIRAL DISCRIMINATION OF DL-AMINO ACIDS BY TRAPPED ION MOBILITY SPECTROMETRY AFTER (+)FLEC DERIVATIZATION

Autores: Raquel Pérez-Míguez [1,2] Elena Domínguez-Vega [2], María Castro-Puyana [1], María Luisa Marina [1], Govert W. Somsen [2]

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2º Premio al mejor Póster (300 euros)

Comunicación: P-42

Título: DIRECT DETERMINATION OF STEROID GLUCURONIDES IN HUMAN URINE BY UHPLC-ESI-(ID)MS/MS AND ISOTOPE PATTERN DECONVOLUTION

Autores: Jorge Pitarch-Motellón [1], Antoni F. Roig-Navarro [1], Oscar J. Pozo [2], María Ibáñez Martínez [1], Juan V. Sancho Llopis [1]

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La entrega de los premios tuvo lugar el 5 de octubre de 2017, durante la ceremonia de clausura de la XVII Reunión Científica de la SECyTA.

Juan Vicente Sancho
Secretario de la SECyTA

1er Premio a la mejor Comunicación Oral (800 euros): comunicación O-YS-08

ION MOBILITY MASS SPECTROMETRY AS A NOVEL TOOL FOR SUPPORTING STEROIDOMICS STUDIES

Maykel Hernández-Mesa (*), Antoine Escourrou, Fabrice Monteau, Gaud Dervilly-Pinel, Bruno Le Bizec

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The global investigation of metabolites (metabolomics) in different fields, including steroids, has resulted in the discovery of new biomarkers highlighting chemical exposures or diseases. Traditionally, GC-MS and LC-MS have been implemented for steroids determination, but these techniques present several disadvantages such as the requirement of derivatization procedures in GC or the low sensitivity observed when ESI is employed. Despite the high selectivity of GC and LC, it cannot be enough for the separation of isomeric steroids, whereas their detection at trace levels in complex matrices can be limited by the presence of chemical noise or matrix interferences. Thus, the unambiguous identification and quantification of certain molecular species can be difficult leading to false assignments. In order to overcome these drawbacks, ion mobility spectrometry (IMS) is proposed as a solution which can be easily included in current analytical workflows. IMS introduces an extra separation dimension allowing the separation of ionized molecules based on their m/z and shape or averaged Collision Cross-Sectional area (CCS). As a result, isomeric and isobaric compounds can be separated based on their structural differences while targeted analytes can be isolated from matrix interferences and background noise. CCS also provides specific information on structural conformation, which can be used as additional identification criteria to retention time and accurate mass when it is orthogonal to *m/z*.

Based on the foregoing, we have investigated the potential of the IMS for steroid determination. This work proposes the first large CCS database for steroids in order to investigate it as additional identification criteria to retention time and accurate mass in LC-IMS-MS analyses. Information for more than 250 steroids, including estrogens, androgens, progestogens and mineralocorticoids, has been included in the proposed database. Although a correlation between *m/z* and CCS can be expected because both are related parameters, it has been observed that several steroids present different CCS than the theoretically predicted one (e.g., trenbolone or dianabol) and CCS defects or excesses are observed. This is especially relevant because CCS can be used as an orthogonal parameter to *m/z* for steroid identification. In addition, the employment of IMS may result crucial for the identification of those analytes which possess the same m/z. IMS allows the separation of isomeric and isobaric compounds, so the consideration of analyte drift times (or their related CCS) in identification assignment workflows, may be a valuable information for achieving higher confidence in the analytical results. As an example, this work proposes the ion mobility separation of several isomer and isobaric pairs such as steroid glucuronides presenting the same *m/z*.

Acknowledgements

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2º Premio a la mejor Comunicación Oral (600 euros): comunicación O-YS-05

USE OF NANOFLOW LIQUID CHROMATOGRAPHY HIGH RESOLUTION MASS SPECTROMETRY FOR THE DETERMINATION OF PESTICIDES IN SPECIFIC PART OF BEES, POLLEN AND NECTAR

David Moreno-González [1,*], Jaime Alcántara-Durán [1], Juan F. García-Reyes [1], Antonio Molina-Díaz [1], Victor Cutillas [2], Amadeo R. Fernández-Alba [2]

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Bees have been an integral part of agriculture for many centuries for the pollination of crops. In fact, approximately 35% of crops depend directly on pollinators. Several studies have proven the role of pesticides in bee deaths and colony collapse disorder. It has been reported that pesticide residues can be accumulated in the pollen and nectar of treated plants, thus posing a potential risk to honey bees. The presence of these residues in nectar and pollen is, therefore, of great concern. The development of analytical methods, which can determine pesticide residues in these types of matrices at very low concentrations, has acquired significant relevance across the globe. On the other hand, to get how pesticide residues can affect bees it is necessary to develop analytical methods, which could detect these compounds in a specific part (abdomen, thorax or head) from one single specimen. Several methods have proposed the use of a pool of bees to obtain enough sample to carry out the sample treatment. However, each bee could have a different content of pesticide residues Nano flow liquid chromatography coupled with electrospray tandem MS can be an interesting alternative to conventional LC methodologies. It provides significant benefits in terms of sensitivity and matrix effects. In this communication, a method based on nanoflow liquid chromatography high resolution mass spectrometry is proposed for the identification and simultaneous quantification of over 100 pesticides in bee parts, nectar and pollen samples. Detection was undertaken with a Thermo Q-Exactive Orbitrap mass spectrometer equipped with an Easy-Spray nano-electrospray ion source. For the separation of the selected pesticides, a Thermo Scientific EASY-nLC 1000 nano-LC system was used. An EASY-Spray column 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 $nL \cdot min^{-1}$. The extraction of pesticides from pollen samples can be performed by modified micro-QuEChERS method. Whereas nectar samples were simply diluted with a solution water-methanol (95/5; v/v), pesticides from bee parts were extracted with MeOH assisted by ultrasound. Good linearity was obtained (greater than 0.999 in all cases). Recoveries for fortified samples ranged from 85% to 97 %, with relative standard deviations lower than 12%. The matrix effect was evaluated for pollen, showing a negligible effect for all studied pesticides, applying a dilution factor of 50. The limits of quantification ranged from 1 to 15 $ng \cdot kg^{-1}$. In addition, a set of real samples were analyzed, obtaining a positive for thiamethoxan in pollen samples (1.3 $\mu g \cdot kg^{-1}$), demonstrating the sensitivity and applicability of the proposed method.

Acknowledgements

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1er Premio al mejor Póster (400 euros): comunicación P-29

FAST CHIRAL DISCRIMINATION OF DL-AMINO ACIDS BY TRAPPED ION MOBILITY SPECTROMETRY AFTER (+)FLEC DERIVATIZATION

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Amino acids (AAs) are a group of organic molecules that play an essential role in the physiology organism. In foods, in addition to the essential proteinogenic AAs, non-protein AAs (more than 800) such as metabolic intermediates, products formed during food processing or additives can be present. Most AAs are chiral molecules. L-AAs are the dominant natural form, but still D-AAs can be found in foods as a consequence of racemization due to food processing, microbiological processes, or fraudulent addition of racemic mixtures in the particular case of supplemented foodstuffs. Therefore, the determination of D-AAs in the food field enables to assess food quality, authenticity and safety.

The most employed analytical techniques to achieve enantiomeric separation of AAs are High Performance Liquid Chromatography, Gas Chromatography and Capillary Electrophoresis. In these techniques, the separation process mostly relies on the use of chiral stationary phases and selectors, and typically take 5-30 min. More recently, Ion Mobility Spectrometry (IMS) has been demonstrated to be a powerful tool for the fast separation of isobaric or isomeric compounds. In IMS, gas phase ions are separated based on their mobility in an electric field through a neutral gas medium in a drift tube. So far, chiral separation of AAs by IMMS has been demonstrated only in few occasions by using a chiral volatile complexing agent, or by forming metal-ion complexes.

In this work, we investigated a new approach for fast chiral AA separation employing Trapped Ion Mobility Spectrometry-Time of Flight Mass Spectrometry (TIMS-TOFMS). DL-AAs were first derivatized with (+)-fluorenylethylchloroformate (FLEC) to form diastereomers and then analyzed by TIMS-TOFMS employing electrospray ionization. Diastereomer mobility resolution could be achieved by adjusting TIMS voltage ramps for individual FLEC-AAs. Na-adduct formation appeared a requirement for separation of the FLEC-AA diasteromers. The D/L migration order was dependent on the structure of the compound. Good enantioresolution was obtained by TIMS for 15 DL-AAs of food interest. Chiral separation of multiple AA in mixtures was shown feasible. This new TIMS-TOFMS methodology can be considered as a promising easy and fast alternative approach for the separation of AA enantiomers.

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2º Premio al mejor Póster (300 euros): comunicación P-42

DIRECT DETERMINATION OF STEROID GLUCURONIDES IN HUMAN URINE BY UHPLC-ESI-(ID)MS/MS AND ISOTOPE PATTERN DECONVOLUTION

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Misuse of steroids is currently a problem of public health. Regarding doping in sports, the detection of the abuse of endogenous anabolic androgenic steroids (EAAS) remains one of the main challenges for doping control laboratories. Currently, the screening of EAAS is based on the inclusion of selected markers in the steroidal module of the Athlete Biological Passport (ABP). These markers are testosterone (T), epitestosterone (E), androsterone (A), etiocholanolone (Etio), 5α-androstane-3α,17β-diol (5αAdiol) and 5β-androstane-3α,17β-diol (5βAdiol) excreted as glucuronide metabolites. The World Anti-Doping Agency (WADA) recommends a procedure which includes an enzymatic hydrolysis, a derivatization step and GC/MS. Alternatively, ultra-high performance liquid chromatography coupled with tandem mass spectrometry (UHPLC-MS/MS), which also shows suitable chromatographic performance and sensitivity, allows for the direct determination of steroid glucuronides by omitting the hydrolysis step. On the other hand, the commonly employed electrospray ionization (ESI) source in LC-MS/MS can suffer ion suppression or enhancement problems hampering the accurate quantification required in EAAS determination. The use of isotope labelled internal standards (ILIS) is widely recognized as the best way to overcome those matrix effect problems. Moreover, isotope pattern deconvolution (IPD) mathematical tool in isotope dilution mass spectrometry (IDMS) circumvents the need of preparing and measuring a calibration curve. It is recognized as a fast, accurate and precise quantification methodology. In the present work, it has been employed for the direct determination of glucuronide metabolites included in the steroidal module of the ABP. After a centrifugation step, urine is fortified with the deuterated analogues, diluted and injected in the UHPLC-ESI-MS/MS instrument.

Separation of the glucuronides has been conducted with a 2.1 x 100 mm, 1.6 µm solid-core particles column. A methanol gradient has been optimized to obtain the baseline separation of EtioG and 5βAdiolG to avoid the mass spectrum overlap between M+2 isotopomer of EtioG and protonated molecule of 5βAdiolG. After successful preliminary results, method validation will be performed with fortified urines at different levels of the six selected glucuronides.