XIV Edición Premios José Antonio García Domínguez

En el marco de la XVIII Reunión Científica de la Sociedad Española de Cromatografía y Técnicas Afines (SECyTA) celebrada en Granada del 2 al 4 de octubre de 2018 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 XIV 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, Núria Fontanals, Begoña Jiménez y Francisco Javier Moreno, 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: Y-01

Título: RAPID IDENTIFICATION OF SYNTHETIC CATHINONES IN SEIZED PRODUCTS TAKING PROFIT OF THE FULL CAPABILITIES OF TRIPLE QUADRUPOLE ANALYSER

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

Comunicación: Y-13

Título: DEVELOPMENT OF A NEW METHODOLOGY FOR THE ANALYSIS OF BIOACTIVE OLIGOSACCHARIDES BY COMPREHENSIVE TWO-DIMENSIONAL HYDROPHILIC INTERACTION×REVERSED PHASE LIQUID CHROMATOGRAPHY

Autores: Andrea Martín [(1)], Ana Isabel Ruiz-Matute [(1)], María Luz Sanz [(1)], Francisco Javier Moreno [(2)], Miguel Herrero [(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), Marta Lores, José A, González Pérez, Belén Gómara Moreno y Alberto Zafra Gómez, tomó por unanimidad los siguientes acuerdos:

1er Premio al mejor Póster (400 euros)

Comunicación: P-OA-01

Título: PRODUCTION AND COMPREHENSIVE CHARACTERIZATION BY LC×LC-PDA-MS OF AQUEOUS PHASES FROM PYROLYSIS OF DIFFERENT BIOMASSES

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2º Premio al mejor Póster (300 euros)

Comunicación: P-OT-08

Título: METABOLOMICS FINGERPRINTING OF BILE SAMPLES IN A CHOLANGIOCARCINOMA STUDY

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La entrega de los premios tuvo lugar el 4 de octubre de 2018, durante la ceremonia de clausura de la XVIII Reunión Científica de la SECyTA.

Juan Vicente Sancho
Secretario de la SECyTA

1er Premio a la mejor Comunicación Oral (800 euros): comunicación Y-01

RAPID IDENTIFICATION OF SYNTHETIC CATHINONES IN SEIZED PRODUCTS TAKING PROFIT OF THE FULL CAPABILITIES OF TRIPLE QUADRUPOLE ANALYSER

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It is undeniable the rising of the so-called "new psychoactive substances" (NPS) in the last decade. The European Monitoring Centre for Drug and Drug Addiction (EMCDDA) recently highlighted the increasing presence of synthetic cathinones in seized products. So, in 2015, out of around 80,000 seizures of NPS reported in Europe, the 33% corresponded to synthetic cathinones. These compounds have similar effects to stimulants drugs such as amphetamines, cocaine and MDMA. They represent the second largest group of NPS controlled by the EMCDDA, with a total of 118 cathinones being currently monitored.

Several LC-based methods have been reported in literature for cathinone identification, being HRMS the preferred technique for identification of active ingredients in seized materials and legal high samples. Different strategies have been described using HRMS, illustrating the tentative identification of cathinones and novel derivatives without the use of reference standards. Nevertheless, the high cost and expensive maintenance of LC-HRMS instruments, together with the complexity of use, make this technique less extended than LC-low-resolution MS/MS in forensic and toxicological laboratories.

In this work, a rapid pseudo-target screening strategy based on monitoring cathinone-typical common fragments and neutral losses has been developed using low-resolution MS/MS. The "pseudo-target" term refers to a methodology developed not for specific compounds (target analysis), but for the detection and tentative identification of a certain family, in this case, synthetic cathinones. In addition, two different sample introduction techniques have been studied: atmospheric solid analysis probe (ASAP) for the direct analysis of the products, and flow-injection analysis (FIA) for extracts. A total of 22 neutral losses and 36 common fragments were acquired and evaluated for cathinone identification. In order to test the approach, 14 blind samples were analysed and the results compared with HRMS data. From the data obtained, the different moieties of the cathinones (and therefore their structure) could be derived, allowing their identification. This methodology will be useful for first, rapid synthetic cathinones detection in laboratories that have low-resolution MS/MS instrumentation.

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2º Premio a la mejor Comunicación Oral (600 euros): comunicación Y-13

DEVELOPMENT OF A NEW METHODOLOGY FOR THE ANALYSIS OF BIOACTIVE OLIGOSACCHARIDES BY COMPREHENSIVE TWO-DIMENSIONAL HYDROPHILIC INTERACTION×REVERSED PHASE LIQUID CHROMATOGRAPHY

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Nowadays, there is a high interest in obtaining bioactive oligosaccharides (OS) to be used as functional components in the food and pharmaceutical industry. Among them, prebiotic OS are in great demand and different commercial formulations can be found in the market. The high complexity of these formulations, with different monomeric units, linkages and degrees of polymerization (DP), makes difficult their characterization and requires the use of analytical techniques with high resolving power and sensitivity. Chromatographic techniques, especially liquid chromatography (LC), have been widely used for OS analysis [1]. However, in the case of complex mixtures, the separation capacity of conventional LC is not enough and the use of multidimensional liquid chromatography, with a higher resolving power, could be an attractive alternative [2]. However, to the best of our knowledge, the application of comprehensive two-dimensional LC (LC×LC) to the analysis of OS mixtures has not yet been performed. Thus, the aim of this work was to develop a new methodology for the analysis of bioactive OS by LC×LC coupled to diode array detection (DAD) and mass spectrometry (MS).

For the method optimization, carbohydrate standards with different DP, monomeric units and linkages were used. Before their analysis, a previous derivatization with 4-aminobenzoic acid ethyl ester (ABEE) was required. LC×LC analyses were carried out on an Agilent 1200 series liquid chromatograph (Agilent Technologies, Santa Clara, CA) equipped with a DAD and an Agilent 6320 Ion Trap mass spectrometer equipped with an electrospray interface. The best orthogonality was achieved using a HILIC XBridge Amide column (2.1 x 150 mm, 3.5 µm particle size) and a partially porous Ascentis Express C_{18} column (50 x 4.6 mm, 2.7 µm particle size), as the first and the second dimension, respectively. Different parameters were also tested such as gradients, flow rates, injection volumes and modulation times. Moreover, the use of active modulation using two C18 trapping columns in the interface was able to efficiently minimize the solvent strength mismatch problems related to this coupling.

The developed methodology was applied to different commercial prebiotic formulations allowing the separation and identification of OS with different structures. To the best of our knowledge, this is the first time that HILIC×RP-LC-DAD-MS has been applied for the analysis of bioactive carbohydrates; based on our results, this could be considered as a powerful analytical technique for the characterization of other OS complex mixtures.

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1er Premio al mejor Póster (400 euros): comunicación P-OA-01

PRODUCTION AND COMPREHENSIVE CHARACTERIZATION BY LC×LC-PDA-MS OF AQUEOUS PHASES FROM PYROLYSIS OF DIFFERENT BIOMASSES

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Pyrolysis is an efficient process for the transformation of biomass into bio-oil (high-added value product). Bio-oil has a complex chemical composition, consisting of water and a hundreds of organic compounds in a two immiscible phases (organic and aqueous) both with potential for the generation of important chemicals for the industry. In order to get improved insight into the composition of the bio-oil, as well to better evaluate their potential applications, detailed chemical analysis techniques are necessary [1,2].

In the case of the organic phase, many papers describing the use of comprehensive two-dimensional gas chromatography (GC×GC) verify the suitability of this technique for this sample. However, for the aqueous phase, due to the unsuitability of water in GC, it is necessary the use of liquid chromatography for the direct analysis of the sample without extraction steps. In this context, a very interesting approach is the use of comprehensive two-dimensional liquid chromatography (LC×LC). The main advantage of this technique compared to 1D-LC is the increased peak capacity due to use different retention mechanisms in each dimension, which is essential for separation of complex mixture, such as the bio-oil aqueous phase [3].

In a previous work [2], fifteen different biomasses were pyrolyzed and their bio-oils were analyzed by GC/MS, but their aqueous phase could not be analyzed by this technique. Thus, the aim of this study is to elucidate the chemical composition of the aqueous phase generated during the pyrolysis of fifteen different biomasses using LC×LC–DAD-MS.

The biomasses evaluated are agro-industrial wastes, which were submitted to a pyrolysis process in a fixed bed reactor with a heating rate of 100 °C min^{-1}, nitrogen flow of 100 mL min^{-1} and final temperature of 650 °C. The phase separation was obtained by simple decantation and the aqueous phase was collected without any further pretreatment or extraction. The aim of this contribution is to optimize a new LC×LC method employing reversed phase separations in both dimensions together with the information provided by DAD and mass spectrometry data to propose a detailed characterization of the entire aqueous phase samples. The total characterization of these samples will aid to confirm their potential use as a source of valuable industrial chemicals.

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[3] L. Monteiro, M. Herrero, E. Ibáñez, A. Cifuentes *J. Chromatogr. A* **1313** (2013) 275-283.

2º Premio al mejor Póster (300 euros): comunicación P-OT-08

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Cholangiocarcinoma (CCA) is the primary hepatic malignancy, despite being a relatively rare cancer. It presents a poor prognosis, a late clinical presentation and, therefore, a high mortality [1]. Currently, advances in metabolomics research are focused on the discovery of potential biomarkers in high-incidence diseases (e.g. cancer), since early diagnosis is mandatory for patient survival. The study of the metabolic profile of bile provides information on the pathogenesis of CCA and allows the identification of biochemical markers of the disease.

A non-targeted metabolomics study based on CE-TOF/MS would be a suitable approach to cover the spectra of ionic and polar metabolites as much as possible. For this purpose, we performed a metabolic fingerprinting study based on bile samples, divided in two groups: six healthy controls (t =16 and t =30 weeks) and seven cases (t = 30). For sample treatment, one volume of bile was mixed with three volumes of cold (−20 °C) ACN. The supernatant was evaporated to dryness and reconstituted in 35 µl of formic acid 0.1 M containing 0.2 mM Methionine Sulfone as the IS. The electropherograms of these samples were overlaid and aligned using specific Agilent software. The features were then filtered by frequency, and subjected to multivariate and univariate data analysis. The robustness of the analysis was tested by the clustering of the QCs observed in a PCA plot, and the differences between groups were investigated by a PLS-DA model. Finally, a tentative identification of those metabolites that were shown to be significantly affected after data reprocessing and statistical analysis was performed across the entire profile. At the end of the process, a chemical identity was assigned to 88 signals by searching their *m/z* against CEU Mass Mediator [2].

In addition, a targeted metabolomics strategy is intended for the detection of relevant candidates. Therefore, a targeted analysis including methionine, glutathione, spermine and cystathionine, among others, was carried out with the aim of identifying the metabolites present in the one-carbon metabolism pathway since its alteration was previously reported by a proteomics study [3].

This metabolomics-based study not only provides a wide metabolic signature to identify potential biomarkers in bile samples of CCA patients but also strengthens the importance of the one-carbon metabolism pathway in the onset and progression of this pathology.

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