XI Edición Premios José Antonio García Domínguez

En el marco de la XV Reunión Científica de la Sociedad Española de Cromatografía y Técnicas Afines (SECyTA) celebrada en Castellón de la Plana del 28 al 30 de octubre de 2015 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 XI 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 Mª García Campaña, Rosa Mª Marcé Recasens y Yolanda Picó García, 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: YS-05

Título: Fingerprinting Analysis of Extracts of Licorice by Comprehensive Two-Dimensional Liquid Chromatograhy

Autores: Lidia Montero[(1)], Elena Ibáñez[(1)], Mariateresa Russo[(2)], Rosa di Sanzo[(2)], Luca Rastrelli[(3)], Anna Lisa Piccinelli[(3)], Rita Celano[(3)], Alejandro Cifuentes[(1)], Miguel Herrero[(1)]

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

Comunicación: YS-04

Título: Classification and Characterization of Mycorrhizal Rosemary Plants by UHPLC-HRMS Compositional Profiles and Chemometrics

Autores: Raquel Seró[(1)], Oscar Núñez[(1)], Javier Saurina[(1)], Cinta Calvet[(2)], Encarnación Moyano[(1)]

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

1er Premio al mejor Póster (400 euros)

Comunicación: P-30

Título: Exploring Potential of Gas Chromatography with Atmospheric Pressure Chemical Ionization and Tandem Mass Spectrometry for Sensitive Determination of Ethyl Glucuronide in Hair

Autores: Tania Portolés[(1)], Juliet Kinyua[(2)], Alexander van Nuijs[(2)], Delphine Cappelle[(2)], Juan V. Sancho[(1)], Félix Hernández[(1)]

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2º Premio al mejor Póster (300 euros)

Comunicación: P-44

Título: UHPLC–API–MS/MS for the Determination of Polyfluorinated Compounds

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La entrega de los premios tuvo lugar el 30 de octubre de 2015, durante la ceremonia de clausura de la XV Reunión Científica de la SECyTA.

Belén Gómara
Secretaria de la SECyTA

1er Premio a la mejor Comunicación Oral (800 euros): comunicación YS-05

FINGERPRINTING ANALYSIS OF EXTRACTS OF LICORICE BY COMPREHENSIVE TWO-DIMENSIONAL LIQUID CHROMATOGRAHY

Lidia Montero[(1)*], Elena Ibáñez[(1)], Mariateresa Russo[(2)], Rosa di Sanzo[(2)], Luca Rastrelli[(3)], Anna Lisa Piccinelli[(3)], Rita Celano[(3)], Alejandro Cifuentes[(1)], Miguel Herrero[(1)]

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Licorice (*Glycyrrhiza glabra*) is an herbaceous perennial plant, belonging to the Leguminosae family and it is one of the oldest and most popular herbal medicines in the world. A wide array of biological activities have been related to this plant, including antiulceric, anti-inflammatory, antispasmodic, expectorant, antiallergic, antidepressive, antiviral and antioxidant activities. Besides, licorice has been used in the food industry as a sweetener and a flavor enhancer.

Glycyrrhiza glabra is native to central and south-western Asia and the Mediterranean region, but the licorice from the region of Calabria (Italy) has been described as one those with highest quality. In order to avoid possible adulterations, it is important to search metabolomic markers that may allow the correct identification of licorice species and varieties. In this regard, the content on secondary metabolites could be employed for the geographical identification of licorice due to fact that the composition of the secondary metabolites in this plant may significantly vary depending on the geographical area of origin. These metabolites present in licorice are mainly triterpene saponins and phenolic compounds including flavanones, chalcones, flavones, isoflavones and isoprenylated flavonoids.

Due to the complex composition of this matrix, chromatographic techniques with high separation power are needed in order to obtain the maximum separation of the compounds.

Therefore, the approach carried out in this work was the development of a comprehensive two-dimensional liquid chromatography method coupled to mass spectrometry (LC x LC-MS IT) for the analysis of licorice extracts from Iran, China and Azerbaijan, as well as two Italian licorices from the region of Calabria, combining ZIC-HILIC and C_{18} columns in the first and second dimension, respectively. The objective was to establish specific compounds that contribute to the differentiation between samples of different geographical origins.

The results of this work revealed that each sample presented several unique compounds in its metabolic profile. The Chinese licorice was the most different of the analyzed samples, followed by the Azerbaijani and the Iranian samples. While the two Italian licorices were the most similar samples. In conclusion LC x LC has been shown to be able to provide complex metabolic prolife useful to reveal specific unique compounds from each sample that could be effectively used as metabolic markers to identify the licorice origin.

ACKNOWLEDGEMENT

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2º Premio a la mejor Comunicación Oral (600 euros): comunicación YS-04

CLASIFICATION AND CHARACTERIZATION OF MYCORRHIZAL ROSEMARY PLANTS BY UHPLC-HRMS COMPOSITIONAL PROFILES AND CHEMOMETRICS

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Rosemary (*Rosmarinus officinalis*) is an aromatic shrub herb that grows wild in the Mediterranean basin. This plant is cultivated worldwide due to its diverse uses as household culinary spice for flavoring, preparation of cosmetic fragrances and in phytotherapy. Furthermore, the antimicrobial and antioxidant properties of rosemary essential oil are of great interest in food, cosmetic and pharmaceutical industries. In addition, long-term studies have shown that scrubland and shrubs contribute to reduction of erosion and improvement of soil quality in Mediterranean environment, and plants with economic potential, such as rosemary, could have an important role in soil rehabilitation and remediation.

R. officinalis colonized with several arbuscular mycorrhizal (AM) fungi have been used for the reclamation of low-nutrient-content soils [1]. These studies revealed that inoculation with AM fungi positively affect rosemary plant growth helping in a better capacity to compete for light with the spontaneous vegetation. Moreover, it is believe that the symbiosis between plant and fungi could alter the composition of plant metabolome, particularly of polyphenols which are the main bioactive compounds in rosemary.

The aim of this work is to explore a suitable methodology to assess the differences between non-inoculated and AM fungi inoculated *R. Officinalis* plants. The characterization and classification can be tackled from compositional profiles as a source of analytical information [2]. For this purpose, a UHPLC-HRMS and UHPLC-MS/HRMS (Q-Orbitrap) using C18 reversed-phase separation has been proposed for the analysis of 10 non-inoculated (control samples) and 50 mycorrhizal rosemary plants (inoculated with 5 different fungi isolates, 10 rosemary plants per fungi).

Full scan MS raw data were employed as metabolic fingerprints to be treated by principal components analysis (PCA), and an interesting pattern distribution regarding the different mycorrhizal and no-mycorrhizal plants was observed. Furthermore, polyphenolic profiles were also employed for rosemary characterization. Thus, MS data was processed by Exact Finder 2.0 software (Thermo Fischer Scientific) by applying a target home-made database with more than 400 polyphenols. Retention time, accurate mass measurements, isotopic pattern fit and product ion scan spectra were used to identify and confirm the compounds when necessary. Finally, the most remarkable polyphenols that allowed the classification were identified and selected to achieve the R. Officialus characterization.

[1] A. Camprubi, I.A. Zárate, A. Adholeya, P. E. Lovato, C. Calvet, Land Degrad. Develop (2013) DOI: 10.1002/ldr.2229
[2] J. Saurina, Trends in Analytical Chemistry 29 (2010) 1027-1037

1er Premio al mejor Póster (400 euros): comunicación P-30

EXPLORING POTENTIAL OF GAS CHROMATOGRAPHY WITH ATMOSPHERIC PRESSURE CHEMICAL IONIZATION AND TANDEM MASS SPECTROMETRY FOR SENSITIVE DETERMINATION OF ETHYL GLUCURONIDE IN HAIR

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The detection and quantification of alcohol consumption is of significance in both forensic and clinical settings and can have a large impact on future legal actions and/or healthcare decisions. A few examples include the legal decisions made concerning the custody of children or the removal of a patient from the liver transplant list, among others [1].

Ethyl glucuronide (EtG) is a minor metabolite of ethanol that accumulates in hair and has proved to be a specific and sensitive long-term biomarker for the detection of chronic and excessive alcohol consumption. Due to the typical wide detection window of the hair matrix and the possibility of segmentation, the evaluation of alcohol consumption in different periods is feasible which constitutes a substantial advantage from routine methods in blood and urine [2].

The metabolization of ethanol to EtG represents approximately 0.05% of the total alcohol elimination and it is excreted mainly in urine providing EtG concentrations in the lower picogram range: >30 pg/mg hair in alcohol-dependent individuals, between 7 and 30 pg/mg hair for moderate alcohol consumers, and <7 pg/mg hair for teetotalers. Sensitive analytical methods are thus required for the reliable determination of such low EtG concentrations.

The current methods offer limits of quantification (LOQs) varying between 2 and 5000 pg/mg with LOQs generally higher (>10 pg/mg hair) for liquid chromatography (LC) methods compared to gas chromatography (GC) methods (<10 pg/mg hair) being better by the use of negative ion chemical ionization (NICI) instead of electron impact (EI), mainly due to the high fragmentation degree of EtG in EI source.

The aim of this work is to explore the capabilities of the recently revived atmospheric pressure chemical ionization source (APCI) in combination with GC and triple quadrupole mass spectrometer for the sensitive quantification of EtG in hair samples after pentafluoropropionic anhydride (PFPA) derivatization. A higher sensitivity would allow a simpler and cheaper preparation step. Soft ionizaton of this source allowed to form [M+H]+ as the base peak of APCI mass spectra, giving the possibility of selecting it as a precursor ion for MS/MS experiments. Matrix matched calibration curve in the range of 1 pg/mg to 250 pg/mg hair was injected in order to check matrix effects and estimate a LOQ and LOD. Obtained results have been compared with GC-NCI-MS/MS.

[1] C.L. Crunelle, M. Yegles, A.L.N. van Nuijs, A. Covaci, et al., Drug and alcohol depend. 134 (2014) 1-11
[2] D. Cappelle, H. Neels, M. Yegles, J. Paulus, A.L.N. van Nuijs, A. Covaci, et al, Forensic Sci. Int. 249 (2015) 20–24

2º Premio al mejor Póster (300 euros): comunicación P-44

UHPLC–API–MS/MS FOR THE DETERMINATION OF POLYFLUORINATED COMPOUNDS

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Fluorotelomers are fluorocarbon–based oligomers partially saturated by fluoride ions which present hydrophilic groups (alcohol, sulfonamide and sulfonamido ethanol). The concern over these compounds has been increased because their widespread in consumer products and their facility to metabolize into the environmentally toxic and persistent perfluorinated carboxylic acid (PFOA) or sulfonates (PFOS) [1].
Gas chromatography coupled to mass spectrometry (GC–MS) is the analytical technique use to analyze fluorotelomers due to their volatile and neutral character, although electron ionization and chemical ionization show some sensitivity problems [2] when analyzing these compounds. Since PFOS and PFOA are ionic compounds, generally determined by liquid chromatography coupled to tandem mass spectrometry (LC–MS/MS), it would be interesting to explore the possibility of analyzing fluorotelomers by LC–MS/MS, in order to make possible the simultaneous determination of the whole family compounds.
In this work, two UHPLC–MS/MS methods are developed using atmospheric pressure chemical ionization (APCI) and atmospheric pressure photoionization (APPI), since ESI was inefficient to ionize fluorotelomers. The UHPLC separation methods were carried out in a C18 column using different mobile phase gradients and the best mobile phase additives that favor the ionization in both APCI and APPI. From fragmentation studies the most intensive and characteristic product ions were selected for quantitative analysis and confirmation purposes when determining these compounds using MRM (multiple reaction monitoring) acquisition mode.
UHPLC–APPI–MS/MS with an acetonitrile–water gradient and post–column addition of toluene as dopant showed 5 times better limits of detection than UHPLC–APCI–MS/MS with a methanol–water gradient. Finally, the selective, sensitive and repetitive UHPLC–APPI–MS/MS method developed has been applied to the analysis of different water samples to evaluate their applicability for environmental monitoring purposes.

[1] H. Fromme, S. Tittlemier, W. Völkel, M Wilhelm, D. Tardella, Int. J. Hyg. Environ. Health 213 (2009) 239-270.
[2] W. M. Herdenson, E. J. Weber, E. Duirk, J. Washington, M. A. Smith, J. Chromatogr. B 846 (2007) 155-161.