BOOK OF ABSTRACTS

XVIII REUNIÓN CIENTÍFICA DE LA SOCIEDAD ESPAÑOLA DE CROMATOGRAFÍA Y TÉCNICAS AFINES · SECyTA 2018

XVIII SCIENTIFIC MEETING OF THE SPANISH SOCIETY OF CHROMATOGRAPHY AND RELATED TECHNIQUES · SECyTA 2018

SECyTA 2018

Granada

www.secyta2018.es

2 - 4 Octubre de 2018

October 2 - 4, 2018

Palacio de Congresos de Granada / *Granada Conference Center*

Organizador
Organizer

SECYTA SOCIEDAD ESPAÑOLA DE CROMATOGRAFÍA Y TÉCNICAS AFINES

Colaboradores
Collaborators

Dpto. de Química Analítica
Prof. Fermín Capitán García

FQM 302

UNIVERSIDAD DE GRANADA

SEEM

BOOK OF ABSTRACTS XVIII SCIENTIFIC MEETING OF THE SPANISH SOCIETY OF CHROMATOGRAPHY AND RELATED TECNIQUES – SECyTA 2018

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BIENVENIDA

En nombre del Comité Organizador de la XVIII Reunión de la Sociedad Española de Cromatografía y Técnicas Afines (SECyTA 2018) queremos daros las gracias por vuestra participación y la bienvenida a la ciudad de Granada y a este foro científico que en esta ocasión tiene lugar en el Palacio de Congresos, en pleno centro de nuestra ciudad.

En esta edición, como en reuniones anteriores, se nos brinda la oportunidad de intercambiar conocimientos científicos y tecnológicos en el ámbito de las técnicas analíticas separativas, contemplando los principales avances en la disciplina, nuevas tendencias instrumentales y multitud de aplicaciones en diversos campos. Además, en colaboración con la Sociedad Española de Espectrometría de Masas (SEEM), como actividad previa a la reunión se ha organizado un curso sobre esta técnica, teniendo como sede la Facultad de Ciencias de la Universidad de Granada, colaboradora de la organización de SECyTA 2018.

El programa científico que desarrollaremos en estos días es denso y muy atractivo e incluirá 6 conferencias plenarias impartidas por científicos de prestigio internacional y 180 comunicaciones, estructuradas en 21 comunicaciones orales y 143 pósteres, de los cuales se han seleccionado 12 para su presentación como “pósteres flash”. Estos trabajos se agrupan en sesiones temáticas dedicadas a análisis clínico y farmacéutico, medioambiental, alimentario, avances en preparación de muestra, fundamentos y quimiometría, nuevos desarrollos en instrumentación y técnicas ómicas, entre otras. Es uno de los mayores intereses de SECyTA promover la participación de los jóvenes investigadores en sus reuniones científicas, fomentando su espíritu crítico y animando a sentirse miembros activos de esta comunidad. Por ello el programa contempla dos sesiones en las que los jóvenes impartirán 16 comunicaciones orales y se han concedido becas de inscripción y ayudas de viaje para facilitar su asistencia. En esta ocasión la XVI Reunión del Grupo Andaluz de la Sociedad Española de Química Analítica (GRASEQA 2018), presidida por el Prof. Luis Fermín Capitán, se celebra coordinadamente con nuestro evento, incorporando una sesión común que permitirá el contacto entre los asistentes de ambas reuniones. Igualmente hemos preparado un programa social con el que disfrutaremos juntos de la ciudad, la tradición y la gastronomía de Granada, metrópolis vibrante, multicultural y por excelencia universitaria, destino acogedor con la Alhambra que domina desde su emplazamiento privilegiado.

Queremos desde aquí expresar nuestro agradecimiento a las empresas que han apoyado activamente la reunión de Granada, presentando sus avances en la exposición comercial, aportando sus productos, presentando comunicaciones y en los encuentros con los participantes, manteniendo un compromiso muy importante con nuestra sociedad.

En nombre del Comité Organizador quiero daros una calurosa bienvenida a Granada, agradeciendo sinceramente vuestra participación y deseando que estos días sean muy provechosos y agradables, personal y profesionalmente.

Ana M. García-Campaña
Presidenta del Comité Organizador

WELCOME

On behalf of the organizing Committee of the XVIII meeting of the Spanish Society of Chromatography and Related Techniques (SECyTA 2018), we want to thank you for your participation and welcome you to the city of Granada and to this scientific forum that this time takes place at the Conference Center, in the heart of our city.

This conference provides an interactive forum to share scientific and technological knowledge in the field of analytical separation techniques. Fundamental aspects and state of the art of chromatography, capillary electrophoresis and related techniques will be discussed. The scientific program includes 6 plenary lectures given by internationally renowned scientists and 180 communications, structured in 21 oral communications and 143 posters, of which 12 have been selected for presentation as "flash posters". These works are grouped in thematic sessions devoted to clinical and pharmaceutical analysis, environmental, food, advances in sample preparation, fundamentals and chemometrics, new developments in instrumentation and omics techniques, among others. It is one of SECyTA's greatest interests to promote the participation of young researchers in their scientific meetings, fostering their scientific spirit and encouraging them to feel active members of this community. For this reason, the program includes two sessions in which young researchers will present 16 oral communications. Also, registration and travel grants have been offered to them.

On this occasion the XVI meeting of the Andalusian group of the Spanish Society of Analytical Chemistry (GRASEQA 2018), chaired by Prof. Luis Fermín Capitan, is held in coordination with our event, incorporating a common session, allowing the contact among the attendees of both meetings. We have also prepared a social program that will allow us to enjoy together the city, the tradition and the gastronomy. We hope that the participants enjoy Granada, a vibrant, multicultural metropolis with an intense university atmosphere. Besides, the visitor can find one of the most visited monuments of Spain, the Alhambra, a 14th century Muslim palace and an absolute must-see attraction.

We want from here to express our gratitude to the companies that have actively supported this meeting, presenting their advances in the commercial exhibition, offering their products, presenting communications and discussing with the participants, maintaining a very important commitment to our society.

On behalf of the organizing committee I want to give you a warm welcome to Granada, sincerely thanking you for your participation and wishing that these days are very profitable, from both sides personal and professionally.

Ana M. García-Campaña
Chair of the Organizing Committee

COMMITTEES INVOLVED IN THE ORGANIZATION OF SECyTA 2018

Conference Chair: Ana M. García Campaña

Secretary: Laura Gámiz Gracia, Francisco J. Lara Vargas, Monsalud del Olmo Iruela

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Universidad Jaume I, Castellón

PREVIOUS MEETINGS

President/s	Location	Year
Jordi Mañes	Valencia	2001
Manuel V. Dabrio	Barcelona*	2002
Amadeo R. Fernández-Alba	Aguadulce (Almería)	2003
Coral Barbas	Boadilla del Monte (Madrid)	2004
Juan Cacho	Barcelona*	2005
Ana Gago	Vigo (Pontevedra)	2006
Ana M. García Campaña	Granada	2007
Joan O. Grimalt	Barcelona*	2008
Carmen Dorronsoro	San Sebastián	2009
Yolanda Picó	Valencia	2010
Elena Domínguez	Barcelona*	2011
Rosa María Marcé	Tarragona	2012
Miguel Ángel Rodríguez y Alejandro Cifuentes	Puerto de la Cruz (Santa Cruz de Tenerife)	2013
Maria José González	Barcelona*	2014
Juan V. Sancho y Joaquín Beltran	Castellón de la Plana	2015
José A. González Pérez	Sevilla	2016
Francisco Javier Santos Vicente	Barcelona*	2017

*Held within the corresponding “Instrumental Analysis Conferences (JAIs)”

INVITED SPEAKERS

Prof. Dr. Robert Kennedy

University of Michigan (USA)
http://kennedygroup.lsa.umich.edu
"Pushing the limits of separations: high speed and high pressure"

Prof. Dr. Soledad Muniategui Lorenzo

Universidad de A Coruña (UDC) – Instituto Universitario de Medio Ambiente (Spain)
http://investigacion.udc.es/es/Research/Details/G000343
"Current Trends in Sample Treatment for Environmental Analysis"

Prof. Dr. Lourdes Ramos

Instituto de Química Orgánica General – CSIC (Spain)
http://www.iqog.csic.es/personal-www/lourdesramos
"Comprehensive two-dimensional gas chromatography-mass spectrometry of complex mixtures: non-orientated studies"

Prof. Dr. Serge Rudaz

School of Pharmaceutical Sciences – University of Geneva (Switzerland)
https://epgl.unige.ch/labs/fanal/analyses-biomedicales
New insights into separation techniques for endogenous metabolomic profiling

Prof. Dr. Oliver J. Schmitz

University of Duisburg-Essen (Germany)
https://www.uni-due.de/aac
"Thousands of separated signals in a four-dimensional separation approach: How can we manage the data?"

Prof. Dr. Antonio Segura Carretero

Universidad de Granada (Spain)
http://www.ugr.es/~agr274/
"Advanced analytical strategies in the field of bioactive ingredients"

TUESDAY, OCTOBER 2nd

8:00 h **Registration**

8:45 h **Opening Ceremony**

Opening Plenary Lecture

Session Chairs: Ana M. García Campaña, University of Granada
Francisco Javier Santos Vicente, University of Barcelona

9:00 h **PL-1** *"Pushing the limits of separations: high speed and high pressure"*
Robert Kennedy
Dept. Chemistry, University of Michigan, Ann Arbor, MI, USA

Oral Session 1 (Clinical and pharmaceutical analysis & Other applications)

Session Chairs: Ana M. García Campaña, University of Granada
Francisco Javier Santos Vicente, University of Barcelona

9:45 h **O1** *"Potential of ion mobility-mass spectrometry for both targeted and untargeted characterisation of phase II steroid metabolites in urine"*
M. Hernández-Mesa, F. Monteau, B. Le Bizec, G. Dervilly-Pinel
Laboratoire d'Etude des Résidus et Contaminants dans les Aliments (LABERCA), Oniris, INRA, Nantes, France

10:05 h **O2** *"LC-MS/MS quantitation of steroid sulfate metabolites to evaluate its potential as markers of testosterone administration"*
A. Esquivel[(1,2)], É. Alechaga[(1)], N. Monfort[(1)], R. Ventura[(1,2)]
[(1)]Catalonian Antidoping Laboratory, Fundació IMIM, Barcelona, Spain; [(2)]Dept. Experimental and Health Sciences, University Pompeu Fabra, Barcelona, Spain

10:25 h **O3** "*Challenges of miniaturizing triple-quadrupole mass spectrometers while maintaining high performance*"
P. Jeanville, S. Tichy, L. Pollum, H. Wang, P. Batoon, J. Bertch, K. Newton
Agilent Technologies, Santa Clara, CA, USA

10:45 h **Coffee break & exhibition** **Poster Session 1 (Clinical and pharmaceutical analysis & Environmental analysis)**

Plenary Lecture

Session Chairs: Esteban Abad Holgado, IDAEA–CSIC, Barcelona
Mª José González Carlos, IQOG–CSIC, Madrid

11:45 h **PL-2** *"Analysis of complex mixtures by comprehensive two-dimensional gas chromatography-mass spectrometry: non-orientated studies"*
Lourdes Ramos Rivero
Dept. Instrumental Analysis and Environmental Chemistry, IQOG-CISC, Madrid, Spain

Oral Session 2 (Environmental analysis)

Session Chairs: Esteban Abad Holgado, IDAEA–CSIC, Barcelona
Mª José González Carlos, IQOG–CSIC, Madrid

12:25 h **O4** *"Target and suspect analytical strategies for the evaluation of contaminants of emerging concern in agricultural soils and crops irrigated with reclaimed wastewater: two years monitoring"*
A. Agüera[(1)], A.B. Martínez-Piernas[(1)], P. Plaza-Bolaños[(1)], P. Fernández-Ibáñez[(2)]
[(1)]CIESOL, Joint Centre University of Almeria-CIEMAT, Almeria, Spain; [(2)]University of Ulster, Newtownabbey, Northern Ireland, United Kingdom

12:45 h **O5** *"Simultaneous analysis of glyphosate and its derivative, (aminomethyl)phosponic acid, in human urine by GC-MS-MS at low ppb levels"*
E. Junqué, P. Fernández, J.O. Grimalt
Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Spain

13:05 h **O6** *"Strategies for target and suspect screening of pharmaceuticals in wastewater effluents using SWATH approach with x500R QTOF"*
N. Montemurro[(1)], D. Barcelo[(1,2)], S. Perez[(1)]
[(1)]Dept. of Environmental Chemistry, Institute for Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Spain; [(2)]Catalan Institute for Water Research (ICRA), Parc Cientific i Tecnològic, University of Girona, Girona, Spain

Young Scientists Session 1 (Clinical and pharmaceutical analysis & Other applications)
Session Chairs: Jordi Díaz Ferrero, IQS–University Ramón Llull, Barcelona
Núria Fontanals Torroja, University Rovira i Virgili, Tarragona

13:25 h **Y1** "*Rapid identification of synthetic cathinones in seized products taking profit of the full capabilities of triple quadrupole analyser*"
D. Fabregat-Safont, J. Vicente Sancho, F. Hernández, M. Ibáñez
Research Institute for Pesticides and Water, University Jaume I, Castellón, Spain

13:35 h **Y2** *"New analytical proposal to monitor volatile organic metabolites as biomarkers of bacterial spoilage in cosmetics"*
M. Celeiro[(1)], E. Varela[(2)], M. Penedo[(2)], R. Rodríguez[(2)], M. Lores[(1)]
[(1)]Dept. Analytical Chemistry, Nutrition and Food Science, Universidade de Santiago de Compostela, Santiago de Compostela, Spain; [(2)]BIOMIG, Hospital Polusa, Lugo, Spain

13:45 h **Y3** "*Combined use of γ-cyclodextrin and chiral ionic liquids for the enantiomeric separation of homocysteine by capillary electrophoresis*"
M. Greño[(1)], M.L. Marina[(1,2)], M. Castro-Puyana[(1,2)]
[(1)]Dept. Analytical Chemistry, Physical Chemistry and Chemical Engineering, University of Alcalá, Alcalá de Henares, Madrid, Spain; [(2)]Institute of Chemical Research "Andrés M. del Río", University of Alcalá, Alcalá de Henares, Madrid, Spain

13:55 h **Lunch** | **14:40 h- 15:25 h** **Coffee seminar (LECO)** "Benefits of GCxGC-TOMS in Food Safety"

15:00 h **Poster Session 2 (Sample preparation & Fundamentals and Chemometrics & Industrial processes)**

Poster Flash Session 1
Session Chairs: Belén Gómara Moreno, IQOG–CSIC, Madrid
Alberto Zafra Gómez, University of Granada

16:00 h **P-CPA-01** "*Creation of a database of human and veterinary drugs containing their collision cross section as novel characterization parameter*"
C. Tejada-Casado[(1)], M. Hernández-Mesa[(2)], F. Monteau[(2)], F.J. Lara[(1)], M. del Olmo-Iruela[(1)], A.M. García-Campaña[(1)], B. Le Bizec[(2)], G. Dervilly-Pinel[(2)]
*[(1)]Dept. Analytical Chemistry, University of Granada, Granada, Spain; [(2)]*LABERCA, Oniris, INRA, Nantes, France

16:05 h **P-CPA-10** *"Bioaccumulation of polycyclic aromatic hydrocarbons in humans. Differentiation between organs using multivariate discriminant analysis"*
M. Pastor-Belda[(1)], P. Viñas[(1)], N. Campillo[(1)], N. Arroyo[(1)], M.D. Pérez-Cárceles[(2)], C. Torres Sánchez[(2)], M. Hernández-Córdoba[(1)]
[(1)]Dept. Analytical Chemistry, University of Murcia, Murcia, Spain, [(2)]Dept. Legal and Forensic Medicine, Biomedical Research Institute (IMIB-Arrixaca), University of Murcia, Murcia, Spain

16:10 h **P-CPA-17** *"Determination of synthetic cathinones in urine by solid-phase extraction followed by liquid chromatography-high resolution mass spectrometry"*
S. Pascual, N. Fontanals, F. Borrull, C. Aguilar, M. Calull
Dept. Analytical Chemistry and Organic Chemistry, University Rovira i Virgili, Tarragona, Spain

16:15 h **P-CPA-18** *"Bioassay-guided isolation of anti-obesity polyphenols from* Lippia citriodora*"*
M.L. Cádiz Gurrea[(1,2)], M. Olivares-Vicente[(3)], M. Herranz-López[(3)], D. Arráez-Román[(1,2)], V. Micol[(3,4)], A. Segura-Carretero[(1,2)]
[(1)]Dept. Analytical Chemistry, University of Granada, Granada, Spain; [(2)]Research and Development of Functional Food Centre (CIDAF), Granada, Spain; [(3)]Institute of Molecular and Cellular Biology (IBMC), University Miguel Hernández, Elche, Alicante, Spain; [(4)]Institute of Health Carlos III (ISCIII), Palma de Mallorca, Spain

16:20 h **P-CPA-19** *"Analytical challenges associated to the control of fashion cosmetics safety"*
L. Rubio, E. Guerra, C. Garcia-Jares, M. Lores
Dept. Analytical Chemistry, Nutrition and Food Science, University Santiago de Compostela, Santiago de Compostela, Spain

16:25 h **P-EA-08** *"IDA and SWATH as non-target acquisition techniques to identify pharmaceuticals in complex environmental matrices"*
R. Alvarez-Ruiz, Y. Picó
Food and Environmental Safety Research Group (SAMA-UV), University of Valencia, Valencia, Spain

16:30 h **Coffee break & exhibition**

Oral Session 3 (Other applications)
Session Chairs: Jordi Díaz Ferrero, IQS–University Ramón Llull, Barcelona
Laura Gámiz Gracia, University of Granada

17:00 h **O7** *"Enatioselective determination of cathinones in urine by high pressure in-line SPE-CE"*
A. Pérez, F. Borrull, M. Calull, C. Aguilar
Dept. Analytical and Organic Chemistry, University Rovira i Virgili, Tarragona, Spain

17:20 h **O8** *"Identification and quantification of volatile NIAS (non intentionally added substances) coming from a starch-base biopolymer intended for food contact by APGC-MS/Q-TOF and GC-MS"*
J. Osorio, A. López, M. Aznar, C. Nerín
Dept. Analytical Chemistry, EINA, University of Zaragoza, Zaragoza, Spain

17:40 h **O9** *"Analysis of allergens in fragrance materials using comprehensive gas chromatography in combination with high resolution time-of-flight mass spectrometry"*
J. Lluch
LECO Sep Science Sales Engineer, Madrid

Young Scientists Session 2 (Environmental analysis & Sample preparation)
Session Chairs: Begoña Jiménez Luque, IQOG–CSIC, Madrid
Monsalud del Olmo Iruela, University of Granada

18:00 h **Y4** *"Flow approaches: automation of sampling and sample preparation as a front end to HPLC"*
D.J. Cocovi-Solberg, M. Miró
Dept. Chemistry, University of the Balearic Islands, Palma de Mallorca, Spain

18:10 h **Y5** *"Bioaccumulation of perfluoroalkyl compounds in marine echinoderms: results of laboratory-scale experiments with* Holothuria tubulosa*"*
J. Martín[(1)], M.T. García Corcoles[(2)], F. Hidalgo[(3)], E. Alonso[(1)], J.L. Vilchez[(2)], A. Zafra-Gómez[(2)]
[(1)]Dept. Analytical Chemistry, University of Seville, Seville, Spain; [(2)]Dept. Analytical Chemistry, University of Granada, Granada, Spain; [(3)]Dept. Zoology, University of Granada, Granada, Spain

18:20 h **Y6** *"Analytical method development for the determination of hydrophilic marine biotoxins in seawater"*
C. Bosch-Orea[(1)], J. Sanchís[(1)], D. Barceló[(1,2)], M. Farré[(1)]
[(1)]Dept. Environmental Chemistry, Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Spain; [(2)]Catalan Institute for Water Research (ICRA), Girona, Spain

18:30 h **Y7** *"A fully automated approach for the analysis of 37 psychoactive substances in wastewater based on on-line SPE-LC-MS/MS"*
E. López-García[(1)], N. Mastroianni[(1)], C. Postigo[(1)], D. Barceló[(1,2)], M. López de Alda[(1)]
[(1)]Dept. Environmental Chemistry, Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Spain; [(2)]Catalan Institute for Water Research (ICRA), Girona, Spain

18:40 h **Y8** *"Layer-by-layer deposition versus electrodeposition to prepare silver-based coatings onto braid solid-phase microextraction fibers for the determination of polycyclic aromatic hydrocarbons in waters"*
A. Gutiérrez-Serpa, D. Schorn-García, V. Pino, F. Jiménez-Moreno, A.I. Jiménez-Abizanda
Dept. Chemistry, University of La Laguna, La Laguna, Spain

19:00 h **Buses from the Congress Center for the Guided visit to the "Albayzin" neighbourhood and Cocktail in "Carmen de la Victoria"**

WEDNESDAY, OCTOBER 3rd

Plenary Lecture
Session Chairs: Joan O. Grimalt Obrador, IDAEA–CSIC, Barcelona
Encarnación Moyano Morcillo, University of Barcelona

9:00 h **PL-3** *"Thousands of separated signals in a four-dimensional separation approach: How can we manage the data?"*
Oliver J. Schmitz
Dept. Applied Analytical Chemistry, Faculty of Chemistry, University of Duisburg-Essen, Germany

Oral Session 4 (New developments in instrumentation)
Session Chairs: Joan O. Grimalt Obrador, IDAEA–CSIC, Barcelona
Encarnación Moyano Morcillo, University of Barcelona

9:45 h **O10** *"Identification and quantification of PCDD/Fs, PCBs and PBDEs in environmental samples using gas chromatography coupled to Orbitrap mass spectrometry"*
J. Parera[(1)], M.G. Martrat[(1)], M.A. Adrados[(1)], J. Sauló[(1)], M. Ábalos[(1)], C.I. Cojocariu[(2)], J. Cooper[(2)], R. Law[(2)], E. Abad[(1)]
[(1)]Laboratory of Dioxins, Environmental Chemistry Department, IDAEA-CSIC, Barcelona, Spain; [(2)]Thermo Fisher Scientific, Runcorn, Cheshire, United Kingdom

10:05 h **O11** "*Potential of lab-in-syringe technique for automated sample pretreatment coupled online to GC-FID"*
B. Horstkotte, P. Solich
Dept. Analytical Chemistry, Charles University, Hradec Králové, Czech Republic

10:25 h **O12** *"Gas chromatography-anion attachment atmospheric pressure photoionization-high resolution mass spectrometry for the determination of short-chain chlorinated paraffins"*
J.F. Ayala-Cabrera, M.T. Galceran, F.J. Santos, E. Moyano
Dept. Chemical Engineering and Analytical Chemistry, University of Barcelona, Barcelona, Spain

10:45 **Coffee break & exhibition** | **Poster session 3 (New developments in instrumentation & Omic techniques & Other applications)**

Plenary Lecture
Session Chairs: Ana M. García Campaña, University of Granada
Juan Vicente Sancho Llopis, University Jaume I, Castellón

11:45 h **PL-4** *"New insights into separation techniques for endogenous metabolomic profiling"*
Serge Rudaz
School of Pharmaceutical Sciences, University of Geneva, Switzerland

Oral Session 5 (Omics techniques & Clinical and Pharmaceutical analysis)
Session Chairs: Ana M. García Campaña, University of Granada
Juan Vicente Sancho Llopis, University Jaume I, Castellón

12:25 h **O13** *"A faster way to electrophoretic mobility: how to enhance the robustness of your CE-MS data with romance"*
V. González-Ruiz[(1,2)], S. Codesido[(1)], N. Drouin[(1)], Y. Gagnebin[(1)], J. Schappler[(1)], S. Rudaz[(1,2)]
[(1)]School of Pharmaceutical Sciences, Universities of Geneva and Lausanne, Switzerland; [(2)]Swiss Centre for Applied Human Toxicology, Switzerland

12:45 h **O14** *"On-line solid-phase extraction capillary electrophoresis-mass spectrometry for the analysis of circulating microRNAs and their post-transcriptional modifications in cancer serum"*
F. Benavente[(1)], R. Pero-Gascon[(1)], M.V. Berezovski[(2)], J. Barbosa[(1)], V. Sanz-Nebot[(1)]
[(1)]Dept. Chemical Engineering and Analytical Chemistry, Institute for Research on Nutrition and Food Safety (INSA·UB), University of Barcelona, Barcelona, Spain; [(2)]Dept. Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Canada

13:05 h **O15** *"A UNIFI-ed solution for high-resolution drug screening"*
P. de la Iglesia
Waters Cromatografía, S.A. Cerdanyola del Vallès, Barcelona, Spain

Young Scientist Sessions 3 (Omic techniques)
Session Chairs: Juan Vicente Sancho Llopis, University Jaume I, Castellón
Francisco Javier Moreno Andújar, CIAL–CSIC, Madrid

13:25 h **Y9** *"CE-MS for metabolome fingerprinting of* Leishmania amazonensis *infected murine macrophages: deciphering L-arginine metabolism"*
M.C. Mamani Huanca[(1)], S. Marcia Muxel[(1,2)], J. Ide Aoki[(2)], R. Andrade Zampieri[(2)], L.M. Floeter-Winter[(2)], C. Barbas[(1)], A. López-Gonzalvez[(1)]
[(1)]Centre of Metabolomics and Bioanalysis (CEMBIO), University San Pablo-CEU; [(2)]Dept. Fisiology, University of São Paulo, São Paulo, SP, Brazil

13:35 h **Y10** *"Study of diabetic nephropathy in HK-2 cells using a metabolomic platform based on liquid chromatography-mass spectrometry"*
S. Bernardo-Bermejo[(1)], E. Sánchez-López[(1)], M. Castro-Puyana[(1,2)], S. Benito[(3)], F.J. Lucio-Cazaña[(3)], M.L. Marina[(1,2)]
[(1)]Dept. Analytical Chemistry, Physical Chemistry and Chemical Engineering, University of Alcalá, Alcalá de Henares (Madrid), Spain; [(2)]Institute of Chemical Research "Andrés M. del Río" (IQAR), University of Alcalá, Alcalá de Henares, Madrid, Spain; [(3)]Dept. Systems Biology, University of Alcalá, Alcalá de Henares, Madrid, Spain

13:45 h **Y11** *"Improving transferrin purification for the detection of aberrant glycosylation in inflammatory diseases"*
M. Mancera-Arteu[(1)], E. Giménez[(1)], J. Sancho[(2)], J. Barbosa[(1)], V. Sanz-Nebot[(1)]
[(1)]Dept. Chemical Engineering and Analytical Chemistry, University of Barcelona, Barcelona, Spain; [(2)]Institute of Parasitology and Biomedicine "López-Neyra" (IPBLN), CSIC, Armilla, Granada, Spain

13:55 h **Lunch** | **14:40 h-15:25 h** **Coffee seminar (AGILENT)** "Estrategias innovadoras para la mejora de su análisis por MS"

15:00 h **Poster Session 4 (Food analysis) & Exhibition**

Poster Flash Session 2
Session Chairs: David Arráez Román, University of Granada
José A. González Pérez, IRNAS-CSIC, Sevilla

16:00 h **P-FA-13** *"Use of combined analytical techniques to prevent labelling fraud of Iberian ham"*
A. Martín-Gómez[(1)], N. Arroyo-Manzanares[(2)], A.I. López-Lorente[(1)], V. Rodríguez-Estévez[(3)], L. Arce[(1)]
[(1)]Dept. Analytical Chemistry, Institute of Fine Chemistry and Nanochemistry, Córdoba, Spain; [(2)]Dept. Analytical Chemistry, University of Murcia, Murcia, Spain; [(3)]Dept. Animal Production, University of Córdoba, Córdoba, Spain

16:05 h **P-FA-26** *"Headspace solid-phase microextraction gas chromatography-mass spectrometry for the determination of semi-volatile fluorinated compounds in microwave popcorn bags"*
A. Contreras-Llin, J.F. Ayala-Cabrera, E. Moyano, F.J. Santos
Dept. Chemical Engineering and Analytical Chemistry, University of Barcelona, Barcelona, Spain

16:10 h **P-FA-28** *"Combined (d)SPE-QuEChERS extraction of mycotoxins in unifeed and analysis by HPLC-HRMS"*
R. Facorro[(1,2)], M. Llompart[(2)], T. Dagnac[(1)]
[(1)]Galician Agency for Food Quality - Agronomic Research Center (AGACAL-CIAM), A Coruña, Spain; [(2)]Laboratory of Research and Development of Analytical Solutions (LIDSA), University of Santiago de Compostela, Santiago de Compostela, Spain

16:15 h **P-FA-37** *"A combined LC-UV-MS and GC-MS approach for authentication of artichoke (*Cynara scolymus*) supplements for overweight control"*
A. Mena, S. Rodríguez, A.I. Ruiz-Matute, A.C. Soria, M.L. Sanz
Institute of General Organic Chemistry (IQOG-CSIC), Madrid, Spain

16:20 h **P-OA-01** *"Production and comprehensive characterization by LC×LC-PDA-MS of aqueous phases from pyrolysis of different biomasses"*
E. Lazzari[(1)], E. Bastos Caramão[(1,2)], M. Herrero[(3)]
[(1)]UFRGS, Institute of Chemistry, Porto Alegre, RS, Brazil; [(2)]UNIT, Programa de Pós-Graduação em Biotecnologia Industrial (PBI), Aracaju, SE, Brazil; [(3)]Dept. Bioactivity and Food Analysis, Institute of Food Science Research (CIAL,CSIC-UAM), Madrid, Spain

16:25 h **P-SP-09** *"Comparative study of three extraction protocols for Viscum album L. proteins"*
M. Vergara-Barberán[(1)], M.J. Lerma-García[(1)], M. Nicoletti[(2)], E.F. Simó-Alfonso[(1)], J.M. Herrero-Martínez[(1)], E. Fasoli[(2)], P. Giorgio Righetti[(2)]
[(1)]Dept. Analytical Chemistry, University of Valencia, Burjassot, Valencia, Spain; [(2)]Dept. Chemistry, Materials & Chemical Engineering "Giulio Natta", Politecnico di Milano, Milan, Italy

16:30 h **Coffee break & exhibition**

Young Scientists Session 4 (Omic techniques & Food analysis)
Session Chairs: Alegría Carrasco Pancorbo, University of Granada
Francisco Javier Moreno Andújar, CIAL–CSIC, Madrid

17:00 h **Y12** *"UHPLC-IMS-QTOF MS metabolomics for biomarker discovery of orange dietary intake"*
L. Lacalle[(1)], T. Portolés[(1)], J.V. Sancho[(1)], F.J. López[(1)], C. Ortega [(2,3)], E.M. Assensio[(2,3)], O. Coltell[(3,4)], D. Corella[(2,3)]
[(1)]Research Institute for Pesticides and Water (IUPA), University Jaume I, Castellón, Spain; [(2)]Dept. Preventive Medicine, University of Valencia, Valencia, Spain; [(3)]CIBER OBN, Institute of Health Carlos III (ISCIII), Madrid, Spain; [(4)]Dept. Computer Languages and Systems, University Jaume I, Castellón, Spain

17:10 h **Y13** *"Development of a new methodology for the analysis of bioactive oligosaccharides by comprehensive two-dimensional hydrophilic interaction×reversed phase liquid chromatography"*
A. Martín[(1)], A.I. Ruiz-Matute[(1)] M.L. Sanz[(1)], F.J. Moreno[(2)], M. Herrero[(2)]
[(1)]Institute of General Organic Chemistry (IQOG-CSIC), Madrid, Spain; [(2)]Institute of Food Science Research (CIAL), CSIC-UAM, Madrid, Spain

17:20 h **Y14** "*Isolation and characterization of A- and B- type of cocoa proanthocyanidins by HPLC-QTOF-MS/MS*"
S. Toro-Uribe[(1)], G. Álvarez-Rivera[(2)], J.A. Perea Villamil[(3)], L. López-Giraldo[(1)], E. Ibáñez[(2)], M. Herrero[(2)]
[(1)]School of Chemical Engineering, Food Science & Technology Research Center (CICTA), Universidad Industrial de Santander, Bucaramanga, Colombia; [(2)]Foodomics Laboratory, Institute of Food Science Research (CIAL, CSIC), Madrid, Spain; [(3)]School of Chemistry, Food Science & Technology Research Center (CICTA), Universidad Industrial de Santander, Bucaramanga, Colombia

17:30 h **Y15** *"Determination of pigments in edible oils by LC-MS: characterization and fraud detection"*
A. Arrizabalaga-Larrañaga[(1)], P. Rodríguez[(2)], M. Medina[(2)], F.J. Santos[(1)], E. Moyano[(1)]
[(1)]Dept. Chemical Engineering and Analytical Chemistry, University of Barcelona, Barcelona, Spain; [(2)]Agri-Food Laboratory, Government of Catalonia, Cabrils, Spain

17:40 h **Y16** *"Analysis of 52 pesticides in fresh fish muscle by dispersive solid phase extraction with QuEChERS followed by UPLC-MS/MS analysis"*
M. Vittoria Barbieri[(1)], C. Postigo[(1)], N. Guillem-Argiles[(1)], L. Simon Monllor-Alcaraz[(1)], J. Izabelle Simionato[(2)], E. Stella[(3)], D. Barceló[(1,4)], M. López de Alda[(1)]
[(1)]Dept. Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain; [(2)]Federal University of Technology, Paraná, Brazil; [(3)]Dept. Civil, Environmental and Mechanical Engineering, University of Trento, Trento, Italy; [(4)]Catalan Institute for Water Research (ICRA), Science and Technology Park, University of Girona, Girona, Spain

Tribute to Prof. Dr. Guillermo Ramis Ramos
Session Chairs: Juan Vicente Sancho Llopis, University Jaume I, Castellón
Francisco Javier Santos Vicente – University of Barcelona

17:50 h **Presentation of the session**. Francisco Javier Santos, President of SECyTA
In memory of Dr. Guillermo Ramis. Maria Celia García Alvárez-Coque
O16 *"Single-pump heart-cutting two-dimensional liquid chromatography applied to the determination of fatty alcohol ethoxylates"*
E.F. Simó-Alfonso, A. Escrig-Domenech, G. Ramis-Ramos
Dept. of Analytical Chemistry, University of Valencia, Valencia, Spain

18:45 h **SECyTA General Assembly**

21:00 h **Cocktail and Conference Dinner at "Carmen de los Chapiteles"**

THURSDAY, OCTOBER 4th

Plenary Lecture (SECyTA & GRASEQA)
Session Chairs: Luis Fermín Capitán Vallvey, University of Granada
Ana M. García Campaña, University of Granada

9:45 h **PL-5** *"Current trends in sample treatment for environmental analysis"*
Soledad Muniategui Lorenzo
University Institute in Environment, University of A Coruña, A Coruña, Spain

Oral Session 6 (Sample preparation & Fundamentals and Chemometrics)
Session Chairs: Belén Gómara Moreno, IQOG–CSIC, Madrid
Núria Fontanals Torroja, University Rovira i Virgili, Tarragona

10:30 h **O17** *"Carbosilane dendrimers and dendrons in protein sample preparation"*
M.C. García[(1)], R. Vásquez-Villanueva[(1)], E. González-García[(1)], E. Hernández-Corroto[(1)], F.J. de la Mata[(2)], M.L. Marina[(1)]
[(1)]Dept. Analytical Chemistry, Physical Chemistry and Chemical Engineering, University of Alcalá, Alcalá de Henares, Madrid, Spain; [(2)]Dept. Organic Chemistry and Inorganic Chemistry, University of Alcalá, Alcalá de Henares, Madrid, Spain

10:50 h **O18** *"UHPLC-ESI-MS/MS and UHPLC-ESI-HRMS in the classification and authentication of Spanish paprika with protected designation of origin by chemometrics"*
S. Barbosa[(1)], G. Campmajó[(1)], O. Núñez[(1,2,3)], J. Saurina[(1,2)], L. Puignou[(1,2)]
[(1)]Dept. Chemical Engineering and Analytical Chemistry, University of Barcelona, Barcelona, Spain; [(2)]Research Institute in Food Nutrition and Food Safety, University of Barcelona, Santa Coloma de Gramanet, Barcelona, Spain; [(3)]Serra Hunter Fellow, Generalitat de Catalunya, Barcelona, Spain

11:10 h **Coffee break & exhibition**

Oral Session 7 (**Food analysis & Fundamentals and Chemometrics**)
Session Chairs: Mª Teresa Galceran Huguet, University of Barcelona
Marta Lores, University of Santiago de Compostela

O19 *"Determination of the content of calystegines in tomato-based products applying LC-HRMS"*
A. Romera-Torres, R. Romero-González, F.J. Arrebola Liébanas, J.L. Martínez Vidal, A. Garrido Frenich
Dept. Chemistry and Physics, Analytical Chemistry Area, University of Almería, Almería, Spain

11:40 h **O20** *"Differentiation of olive oils from the same botanical variety (Arbequina) according to their geographic origin using chromatographic techniques and chemometric tools"*
D.N. Vera[(1)], I. Ruisánchez[(1)], M.P. Callao[(1)], A.M. Jiménez-Carvelo[(2)], L. Cuadros-Rodríguez[(2)]
[(1)]Dept. Analytical and Organic Chemistry, Rovira i Virgili University, Tarragona, Spain; [(2)]Dept. Analytical Chemistry, University of Granada, Granada, Spain

12:00 h **O21** *"Detection and quantification of casein and ovalbumin in Chilean wines with UHPLC/ESI-QQQ-MS/MS and UHPLC-ESI/QTOF-MS/MS"*
J. Pavón[(1)], G. Alvarez[(2)], M. Herrero[(2)], A. Cifuentes[(2)], K. Henriquez[(1,3)], M. Aranda[(1,3)]
[(1)]Dept. Food Science and Technology, University of Concepcion, Concepcion, Chile; [(2)]Institute of Food Science Research (CIAL-CSIC), Madrid, Spain; [(3)]Center for Biotechnology, University of Concepcion, Concepcion, Chile

12:20 h

Closing Plenary Lecture
Session Chairs: Mª Teresa Galceran Huguet, University of Barcelona
Marta Lores Aguín, University of Santiago de Compostela

12:40 h **PL-6** *"Advanced analytical strategies in the field of bioactive ingredients"*
Antonio Segura Carretero
Dept. Analytical Chemistry, University of Granada, Granada, Spain

13:20 h **Closing Ceremony & Awards**

13:45 h **Farewell Cocktail**

TUESDAY OCTOBER 2nd

Poster Session 1:

Clinical and pharmaceutical analysis (CPA) & Environmental analysis (EA)

Clinical and pharmaceutical analysis (CPA)

P-CPA-01 **CREATION OF A DATABASE OF HUMAN AND VETERINARY DRUGS CONTAINING THEIR COLLISION CROSS SECTION AS NOVEL CHARACTERIZATION PARAMETER**
C. Tejada-Casado, M. Hernández-Mesa, F. Monteau, F.J. Lara, M. del Olmo-Iruela, A.M. García-Campaña, B. Le Bizec, G. Dervilly-Pinel

P-CPA-02 **DETECTION OF INTRAMUSCULAR ADMINISTRATION OF TESTOSTERONE IN CAUCASIAN AND ASIAN POPULATION USING STEROID SULFATE METABOLITES**
A. Esquivel, É. Alechaga, N. Monfort, R. Ventura

P-CPA-03 **METABOLITE ELUCIDATION OF TWO SYNTHETIC CANNABINOIDS AFTER POOLED HUMAN HEPATOCYTES INCUBATION**
D. Fabregat-Safont, M. Mardal, J.V. Sancho, P.W. Dalsgaard, F. Hernández, K. Linnet, M. Ibáñez

P-CPA-04 **DEVELOPMENT, VALIDATION AND APPLICATION OF A GC-MS METHOD FOR THE SIMULTANEOUS DETECTION AND QUANTIFICATION OF NEUTRAL LIPID SPECIES IN TRYPANOSOMA CRUZI EPIMASTIGOTE**
M. Santivañez-Veliz, B. Arce, E. Moreno-Viguri, S. Pérez-Silanes, J. Varela, H. Cerecetto, M. González, E. Lizárraga

P-CPA-05 **COMPARISON OF ISOTOPE PATTERN DECONVOLUTION AND CALIBRATION CURVE QUANTIFICATION METHODS FOR THE DETERMINATION OF ESTRONE AND 17β-ESTRADIOL IN HUMAN SERUM**
J. Pitarch-Motellón, N. Fabregat-Cabello, C. Le Goff, A.F. Roig-Navarro, J.V. Sancho Llopis, E. Cavalier

P-CPA-06 **DETERMINATION OF SELECTED METABOLITES OF ENDOGENOUS ANDROGENIC ANABOLIC STEROIDS IN URINE BY LC-MS AND ISOTOPE PATTERN DECONVOLUTION**
S.E. Bedelean, J. Pitarch-Motellón, J.V. Sancho, M. Ibáñez, A.F. Roig-Navarro

P-CPA-07 **APPLICABILITY OF AMBIENT IONIZATION TECHNIQUES FOR THE ANALYSIS OF DRUGS IN URINE**
C. Bressan, R. Seró, E. Alechaga, N. Monfort, E. Moyano, R. Ventura

P-CPA-08 **FEASIBILITY OF GC-APPI-HRMS TO DETECT PHENYLALKYLAMINE STIMULANTS IN SPORTS DRUG TESTING**
C. Bressan, J.F. Ayala-Cabrera, F.J. Santos, S. Cuadras, L. Garrostas, N. Monfort, E. Alechaga, E. Moyano, R. Ventura

P-CPA-09 **TOWARDS AN ENHANCED CHEMICAL STABILITY AND BIOAVAILABILITY OF CAMPTOTHECIN THROUGH THE FORMATION OF CICLODEXTRIN INCLUSION COMPLEXES. A RP-HPLC-FL EVALUATION**
M. A. Martín, A.I. Olives, K. Xiomara Orellana, P. Michalska, I. Buendia, R. León, J.C. Menéndez

P-CPA-10 **IONIC LIQUIDS AS MOBILE PHASE ADDITIVES FOR ENHANCING THE SEPARATION OF ANTICANCER DRUGS BY HPLC WITH FLUORIMETRIC DETECTION**
M. A. Martín, F.M. Silva-Sofrás, A.I. Olives

P-CPA-11 **BIOACCUMULATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN HUMANS. DIFFERENTIATION BETWEEN ORGANS USING MULTIVARIATE DISCRIMINANT ANALYSIS**
M. Pastor-Belda, P. Viñas, N. Campillo, N. Arroyo, M.D. Pérez-Cárceles, C. Torres Sánchez, M. Hernández-Córdoba

P-CPA-12 **DETERMINATION OF NUCLEOTIDES IN SUPPLEMENT FEED USING ION-PAIR LIQUID CHROMATOGRAPHY WITH DUAL ELECTROSPRAY ATMOSPHERIC PRESSURE CHEMICAL IONIZATION TIME-OF-FLIGHT MASS SPECTROMETRY**
N. Campillo, A. Sáez, M. Pastor-Belda, P. Viñas, M. Hernández-Córdoba

P-CPA-13 **SEPARATION AND IDENTIFICATION BY (RP)UHPLC-UV-MS OF FOUR THERAPEUTICAL MONOCLONAL ANTIBODIES**
R. Pérez-Robles, L. Cuadros-Rodríguez, A. Salmerón-García, N. Navas

P-CPA-14 **NATIVE MASS SPECTROMETRIC SIZE EXCLUSION LIQUID CHROMATOGRAPHIC ANALYSIS OF THE MONOCLONAL ANTIBODIES INFLIXIMAB AND BIOSIMILAR CT-P13: AGGREGATES AND INTACT ISOFORMS PROFILES**
R. Pérez-Robles, L. Cuadros-Rodríguez, A. Salmerón-García, J. Cabeza, N. Navas

P-CPA-15 **IS STRONGER ALWAYS BETTER? EFFECT OF URINE FREEZING TEMPERATURE ON PROSTATE SPECIFIC ANTIGEN (PSA) ANALYSIS BY CAPILLARY ELECTROPHORESIS IN THE SEARCH OF PROSTATE CANCER MARKERS.**
D. Navarro-Calderón, A. Puerta, B. Limones, J.C. Diez-Masa, M. de Frutos

P-CPA-16 **CAPILLARY ELECTROPHORESIS IN COMBINATION WITH FIELD AMPLIFIED SAMPLE INJECTION FOR THE DETERMINATION OF TETRACYCLINES IN HUMAN URINE SAMPLES**
D. Moreno-González, M. Krulišová, L. Gámiz-Gracia, A.M. García-Campaña

P-CPA-17 **DETERMINATION OF SYNTHETIC CATHINONES IN URINE BY SOLID-PHASE EXTRACTION FOLLOWED BY LIQUID CHROMATOGRAPHY-HIGH RESOLUTION MASS SPECTROMETRY**
S. Pascual, N. Fontanals, F. Borrull, C. Aguilar, M. Calull

P-CPA-18 **BIOASSAY-GUIDED ISOLATION OF ANTI-OBESITY POLYPHENOLS FROM *LIPPIA CITRIODORA***
M.L. Cádiz Gurrea, M. Olivares-Vicente, M. Herranz-López, D. Arráez-Román, V. Micol, A. Segura-Carretero

P-CPA-19 **ANALYTICAL CHALLENGES ASSOCIATED TO THE CONTROL OF FASHION COSMETICS SAFETY**
L. Rubio, E. Guerra, C. Garcia-Jares, M. Lores

Environmental analysis (EA)

P-EA-01 **VALIDATION STUDY OF AN ON-LINE ANALIZER FOR THE DETERMINATION OF TRIHALOMETHANES IN DISTRIBUTION DRINKING WATER ACCORDING TO ISO 17025**
G. Carrera, M. West, M.R. Boleda, L. Vázquez

P-EA-02 **DIRECT DETERMINATION OF ULTRATRACE TOTAL INORGANIC IODINE IN SEAWATER BY LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY**
M. Hernáiz-Izquierdo, P. Galindo-Iranzo, M.P. García-Armada, A. Saiz-López, B. Gómara, R. Lebrón-Aguilar, J.E. Quintanilla-López

P-EA-03 **CHARACTERIZATION OF THE ORGANOHALOGENATED BURDEN IN INFERTILE MILVUS MIGRANS EGGS FROM A CONTAMINATED AREA IN MADRID (SPAIN)**
J. Berges-Castanera, J. Escobar-Arnanz, E. Eljarrat, G. Blanco, L. Ramos

P-EA-04 **MULTI-RESIDUE ANALYSIS OF 22 CONTAMINANTS OF EMERGING CONCERN IN RIVER WATER BY LARGE VOLUME DIRECT INJECTION-LIQUID CHROMATOGRAPHY TANDEM MASS SPECTROMETRY**
J. Borrull, A. Colom, J. Fabregas, E. Pocurull, F. Borrull

P-EA-05 **ACT MICROPLASTICS AS CONCENTRATORS OF ORGANIC POLLUTANTS SUSPENDED IN WATER? FOR EXAMPLE, PBDEs**
M. Singla, S. Borrós, F. Broto, J. Díaz

P-EA-06 **DIRECT DETERMINATION OF POLYCHLORINATED BIPHENYLS IN SOLID AND SEDIMENTS BY THERMAL DESORPTION-GAS CHROMATOGRAPHY-MASS SPECTROMETRY**
L. Corell, S. Armenta, M. de la Guardia, F.A. Esteve-Turrillas

P-EA-07 **BIOFERTILIZATION OF VINEYARDS: INFLUENCE OF VERMICOMPOST IN THE POLYPHENOLIC PROFILE OF GALICIAN WINES**
L. Rubio, J. Domínguez, J.P. Lamas, M. Celeiro, C. Garcia-Jares, M. Lores

P-EA-08 **IDA AND SWATH AS NON-TARGET ACQUISITION TECHNIQUES TO IDENTIFY PHARMACEUTICALS IN COMPLEX ENVIRONMENTAL MATRICES**
R. Álvarez-Ruiz, Y. Picó

P-EA-09 **ANALYSIS OF PESTICIDE RESIDUES IN HONEYBEES, POLLEN AND BEESWAX BY QUECHERS EXTRACTION AND LC-MS/MS DETERMINATION**
P. Calatayud-Vernich, F. Calatayud, E. Simó, Y. Picó

P-EA-10 **EFFECT OF CLIMATIC VARIABILITY IN THE SOIL ORGANIC MATTER COMPOSITION STUDIED BY ANALYTICAL PYROLYSIS**
M.A. Jiménez-González, J.M. de la Rosa, J.A. González-Pérez, A.M. Álvarez, P. Carral, G. Almendros

P-EA-11 **ANALYTICAL CHALLENGES OF ANALYSIS OF POLLUTANT INCLUDED IN "WATCH LISTS OF WATER FRAMEWORK DIRECTIVE" BY LC-MS/MS AND HRMS**
E.M. Herrera, C. Flores, A. Bartolomé, J. Caixach

P-EA-12 **DETERMINATION OF HIGH VOLUME PRODUCTION CHEMICALS IN OUTDOOR AIR PARTICULATE MATTER. ASSESSING THE HUMAN EXPOSURE**
A. Maceira, I. Pecikoza, R.M. Marcé, F. Borrull

P-EA-13 **APPLYING LC-HR-MS SUSPECT SCREENING FOR THE DETECTION OF PHOTOTRANSFORMATION PRODUCTS OF PHARMACEUTICALS IN SURFACE WATERS**
S. Pérez, M. García-Vara, D. Barceló, N. Montemurro

P-EA-14 **CATIONIC AMINE-BRIDGED PERIODIC MESOPOROUS ORGANOSILICA MATERIALS FOR OFF-LINE SOLID-PHASE EXTRACTION OF PHENOXY ACID HERBICIDES FROM WATER SAMPLES PRIOR TO THEIR SIMULTANEOUS ENANTIOMERIC DETERMINATION BY CAPILLARY ELECTROPHORESIS**
J. Valimaña-Traverso, S. Morante-Zarcero, D. Pérez-Quintanilla, M.A. García, I. Sierra, M.L. Marina

P-EA-15 **SIMULTANEOUS ENANTIOMERIC DETERMINATION OF DRUGS IN WATER SAMPLES BY CAPILLARY ELECTROPHORESIS AFTER SOLID-PHASE EXTRACTION WITH PERIODIC MESOPOROUS ORGANOSILICA MATERIALS**
J. Valimaña-Traverso, S. Morante-Zarcero, D. Pérez-Quintanilla, M.A. García, I. Sierra, M.L. Marina

P-EA-16 **ASSESSMENT OF POPs IN MARINE MAMMALS FROM THE MEDITERRANEAN SEA**
J. Muñoz-Arnanz, A. Bartalini, F. Capanni, L. Marsili, C. Fossi, B. Jiménez

P-EA-17 **PRESENCE AND ELIMINATION OF CONTAMINANTS OF EMERGING CONCERN THROUGH A TREATMENT LINE FOR LANDFILL LEACHATE REMEDIATION**
A. Ruíz-Delgado, P. Plaza-Bolaños, S. Malato, I. Oller, A. Agüera

P-EA-18 **DIFFERENT TYPES OF SOLID PHASE EXTRACTION FOR ABOUT 30 ORGANIC COMPOUNDS, SUCCESSIVELY DETERMINED BY HPLC/MS-MS (QqQ)**
D. Sadutto, P. Calatayud-Vernich, Y. Picó

P-EA-19 **MONITORING OF CYANOTOXINS IN WATER BY ULTRA-HIGH PERFORMANCE LIQUID CHROMATOGRAPHY FOLLOWING SALTING-OUT ASSISTED LIQUID-LIQUID EXTRACTION**
M. Hemmati, C. Tejada-Casado, M.C. Contreras-Morales, F.J. Lara, M. Rajabi, A.M. García-Campaña, M. del Olmo-Iruela

P-EA-20 **EMERGING POLLUTANTS IN SOIL AND PLANTS OF SAUDI ARABIA: CONSEQUENCES OF THE USE OF TREATED WASTE WATER FOR IRRIGATION**
R. Alvarez-Ruiz, Y. Picó, L. Wijaya, A.H. Alfarhan, M. Alyemeni, D. Barceló

P-EA-21 **COMBINED GC-MS AND CHEMOMETRIC APPROACH FOR THE COMPREHENSIVE ANALYSIS OF ORGANIC COMPOUND SOURCES IN RURAL AND URBAN ATMOSPHERES**
B.L. van Drooge, E. Marco, J.O. Grimalt

P-EA-22 **MICROPLASTIC POLLUTION IN THE ATLANTIC OCEAN: IDENTIFICATION OF POLYMER TYPES AND ADDITIVE CONTENT USING ANALYTICAL PYROLYSIS (PY-GC/MS)**
J.A. González-Pérez, L.M. San Emeterio, B. Abaroa Pérez, D. Vega Moreno

P-EA-23 **ANALYTICAL PYROLYSIS OF SOIL EASILY-EXTRACTABLE GLOMALIN (EEG) FRACTION**
E. Lozano, J. Mataix-Solera, V. Arcenegui, L.M. San Emeterio, J.A. González-Pérez

P-EA-24 **ANALYSIS OF POLYSTYRENE MICROPLASTICS BY LC-QEXACTIVE ORBITRAP IN COASTAL AREAS OF CATALONIA**
G.F. Schirinzi, M. Llorca, D. Barceló, M. Farré

P-EA-25 **SUBCRITICAL WATER COMBINED WITH MEMBRANE ASSISTED EXTRACTION FOR ATMOSPHERIC PARTICLE-BOUND PAHs DETERMINATION**
C. Ramos Contreras, E. Concha-Graña, P. López-Mahía, F. Molina-Pérez, S. Muniategui-Lorenzo

P-EA-26 **COMPARATIVE RESPONSE TO TAMIFLU® (OSELTAMIVIR PHOSPHATE) UNDER WATER-EXPOSURE IN MUSSELS AND CLAMS**
S. Dallarés, N. Montemurro, S. Pérez, N. Rodríguez-Sanchez, M. Solé

P-EA-27 **MULTIRESIDUE ANALYSIS OF PERSONAL CARE PRODUCTS IN CONTINENTAL WATERS BY SOLID-PHASE MICROEXTRACTION-GAS CHROMATOGRAPHY TRIPLE QUADRUPOLE MASS SPECTROMETRY**
C. Garcia-Jares, M. Vila, M. Celeiro, J.P. Lamas, V. Homem, N. Ratola, M. Llompart

P-EA-28 **DETERMINATION OF NEONICOTINOID INSECTICIDE RESIDUES IN WATER SAMPLES BY MICELLAR ELECTROKINETIC CAPILLARY CHROMATOGRAPHY**
L. Carbonell-Rozas, J.E. Cejas-Aguilar, A.M. García-Campaña, F.J. Lara

P-EA-29 **STRUCTURE OF BIOCHARS PRODUCED FROM HYDROTHERMAL CARBONIZATION AND PYROLYSIS OF ORGANIC WASTE AND THEIR POTENTIAL USE AS N FERTILIZERS**
J.M. De la Rosa, M. Paneque, M.A. Jiménez-González, N.T. Jiménez-Morillo, P. Campos, F. González-Vila, H. Knicker

P-EA-30 **ANALYSIS OF POLYESTIRENE BASED MICROPLASTICS IN ENVIRONMENTAL SAMPLES**
M. Farré, G. Schirinzi, M. Llorca, E. Abad, D. Barceló

Poster Session 2:

Sample preparation (SP) & Fundamentals and Chemometrics (FCH) & Industrial processes (IP)

Sample preparation (SP)

P-SP-01 **DETERMINATION OF PHENOLIC COMPOUNDS IN TEA BY USING CYCLODEXTRIN-METHACRYLATE HYBRID MONOLITHIC MATERIALS**
C. Belenguer-Sapiña, E. Pellicer-Castell, A. Mauri-Aucejo, P. Amorós, E.F. Simó-Alfonso, C. Vila

P-SP-02 **SYNTHESIS OF GROUND POLYMERIC SORBENTS WITH CYCLODEXTRIN NANOPARTICLES FOR ANALYTICAL APPLICATIONS**
A. Mauri-Aucejo, E. Pellicer-Castell, C. Belenguer-Sapiña, P. Amorós, E.F. Simó-Alfonso, C. Vila

P-SP-03 **AUTHOMATED DETERMINATION OF INSECTICIDE METABOLITES IN URINE SAMPLES BY TURBOFLOW-LIQUID CROMATOGRAPHY COUPLED TO ORBITRAP MASS SPECTROMETRY**
M. López García, A. Romera-Torres, R. Romero González, A. Garrido Frenich

P-SP-04 **EXTRACTION AND DETERMINATION OF AFLATOXINS IN FOOD SAMPLES BY USING A NOVEL MESOPORUS SILICA-BASED SORBENT**
E. Pellicer-Castell, C. Belenguer-Sapiña, N. Puertes-Espadas, A. Mauri-Aucejo, P. Amorós

P-SP-05 **MOLECULARLY-IMPRINTED POLYMER-STIR CAKE SORPTIVE EXTRACTION OF ECGONINE METHYL ESTER FROM WATER AND BIOLOGICAL SAMPLES FOR THE EVALUATION OF COCAINE ABUSE**
R. Arraez, A. Sorribes-Soriano, J.M. Herrero-Martínez, S. Armenta, F.A. Esteve-Turrillas

P-SP-06 **ION MOBILITY SPECTROMETRY DETERMINATION OF DICHLOROPANE IN ORAL FLUID BY MICROEXTRACTION BY PACKED SORBENT**
A. Monedero, F.A. Esteve-Turrillas, S. Armenta

P-SP-07 **MOLECULARLY-IMPRINTED PIPETTE-TIP EXTRACTION OF AMPHETAMINE-TYPE SUBSTANCES FROM ORAL FLUIDS**
A. Valencia, A. Sorribes-Soriano, J.M. Herrero-Martínez, S. Armenta, F.A. Esteve-Turrillas

P-SP-08 **EVALUATION OF GREEN ASPECTS OF ANALYTICAL TECHNOLOGY BASED ON DEEP EUTECTIC SOLVENTS FOR EXTRACTION OF BIOACTIVE COMPOUNDS FROM OLIVE LEAF**
M. Elena Alañón, A.M. Gómez-Caravaca, D. Arráez-Román, A. Segura-Carretero

P-SP-09 **COMPARATIVE STUDY OF THREE EXTRACTION PROTOCOLS FOR *VISCUM ALBUM L.* PROTEINS**
M. Vergara-Barberán, M.J. Lerma-García, M. Nicoletti, E.F. Simó-Alfonso, J.M. Herrero-Martínez, E. Fasoli, P.G. Righetti

P-SP-10 **MOLECULARLY IMPRINTED MACROPOROUS MONOLITHIC MATERIALS FOR SELECTIVE RECOGNITION OF HUMAN SERUM ALBUMIN**
M. Vergara-Barberán, I.M. Fombella-Gracía, E.F. Simó-Alfonso, J.M. Herrero-Martínez

P-SP-11 **APTAMER-MODIFIED MONOLITHIC CAPILLARY COLUMNS FOR HIGHLY SELECTIVE RECOGNITION OF ALLERGENIC PROTEINS**
M. Vergara-Barberán, E.F. Simó-Alfonso, J.M. Herrero-Martínez

P-SP-12 **IMPROVING FRACTIONATION OF HUMAN MILK PROTEINS THROUGH CALCIUM PHOSPHATE CO-PRECIPITATION AND THEIR RAPID ANALYSIS BY CAPILLARY ELECTROPHORESIS**
I. Ten-Doménech, E.F. Simó-Alfonso, J.M. Herrero-Martínez

P-SP-13 **POLY(ETHYLENE GLYCOL) DIACRYLATE-BASED GROUND MONOLITHIC SORBENT FOR DETERMINATION OF SULFONAMIDES IN DIFFERENT MATRICES**
M. Vergara-Barberán, A. Moga, H. Martínez-Pérez-Cejuela, J.M. Herrero-Martínez, E.F. Simó-Alfonso

P-SP-14 **DEVELOPMENT OF MINIATURIZED SYSTEMS BASED ON POLYMERIC SORBENTS MODIFIED WITH GOLD NANOPARTICLES FOR AMINOTHIOLS ANALYSIS IN BIOLOGICAL SAMPLES**
O. Mompó-Roselló, J. Rojo-Fernández, J.M. Herrero-Martínez, E. Simó-Alfonso

P-SP-15 **A MODIFIED QUECHERS METHOD FOR THE DETERMINATION OF TETRACYCLINES IN FISH MUSCLE BY UHPLC–MS/MS**
D. Moreno-González, A. Grande-Martínez, F.J. Arrebola-Liébanas, A. Garrido-Frenich, A.M. García-Campaña

P-SP-16 **OPTIMIZATION OF THE EXTRACTIONS BY SUPERCRITICAL FLUIDS AND PRESSURIZED LIQUID EXTRACTION FROM DATE FRUIT**
S. Jazi, J.A. Mendiola, A. Cherif, W. Mnif, E. Ibañez

P-SP-17 **CLOUD POINT EXTRACTION FOR DETERMINATION OF VITAMIN D AND THEIR METABOLITES IN HUMAN URINE USING LIQUID CHROMATOGRAPHY WITH TANDEM MASS SPECTROMETRY**
M. Pastor-Belda, S. Requena, N. Campillo, P. Viñas, N. Arroyo, M. Hernández-Córdoba

P-SP-18 **SUPERCRITICAL FLUID EXTRACTION AND CHEMICAL CHARACTERIZATION OF TERPENES OBTAINED FROM OLIVE LEAVES**
Z. Suárez Montenegro, G. Álvarez-Rivera, J.A. Mendiola, A. Cifuentes, E. Ibáñez

P-SP-19 **EVALUATION OF NEW PROTEOLYTIC ENZYMES TO PRODUCE HYPOCHOLESTEROLEMIC PEPTIDES FROM OLIVE SEED PROTEINS**
I.M. Prados-Nieto, E. Domínguez-Vega, M.L. Marina, M. Wuhrer, M.C. García

P-SP-20 **AUTOMATION OF SINGLE-DROP EXTRACTION APPROACHES BASED ON THE LAB-IN-SYRINGE TECHNIQUE**
I.H. Šrámková, B. Horstkotte, H. Sklenářová, P. Solich

P-SP-21 **MINIATURIZED DISPERSIVE SOLID-PHASE EXTRACTION USING A NOVEL METAL-ORGANIC FRAMEWORK CIM-81 AS SORBENT FOR THE EXTRACTION OF PERSONAL CARE PRODUCTS IN ENVIRONMENTAL WATERS**
P. González-Hernández, A.B. Lago, J.H. Ayala, J. Pasán, C. Ruíz-Pérez, V. Pino, A.M. Afonso

P-SP-22 **NOVEL METAL ORGANIC FRAMEWORK-BASED SOLID-PHASE MICROEXTRACTION FIBERS: IMPORTANCE OF SUPPORT TREATMENT**
P. Rocío-Bautista, J.H. Ayala, A.M. Afonso, J. Pasán, C. Ruiz-Pérez, V. Pino, R. Ameloot

P-SP-23 **MINIATURIZED DISPERSIVE SOLID-PHASE EXTRACTION VERSUS MINIATURIZED STATIC SOLID-PHASE EXTRACTION USING AS SORBENT CORE-SHELL MICROPARTICLES OF THE METAL ORGANIC FRAMEWORK CIM-80 (CIM-80@SiO2) FOR THE EXTRACTION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM WATERS**
A. Gutiérrez-Serpa, V. Pino, J. Pasán, F. Jiménez-Moreno, A.I. Jiménez-Abizanda, C. Ruíz-Pérez

P-SP-24 **UNSUPERVISED IN-VITRO MONITORING OF THE LEACHING KINETICS OF EMERGING CONTAMINANTS FROM MICROPLASTICS IN THE MARINE ENVIRONMENT BY ON-LINE COUPLING OF MINI-COLUMN EXTRACTION TO HPLC**
K. Fikarova, D.J. Cocovi-Solberg, M. Rosende, B. Horstkotte, H. Sklenářova, M. Miró

P-SP-25 **EVALUATION OF IN-HOUSE SYNTHESIZED POLYMERIC SORBENT WITH ZWITTERIONIC CHARACTER FOR THE SIMULTANEOUS SOLID-PHASE EXTRACTION OF ACID, BASIC AND AMPHOTERIC ANALYTES**
J.C. Nadal, F. Borrull, P.A.G. Cormack, R.M. Marcé, N. Fontanals

Fundamentals and Chemometrics (FCH)

P-FCH-01 **DEVELOPMENT OF A RETENTION TIME INDEX FOR LIQUID CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY IN BOTH POSITIVE AND NEGATIVE IONIZATION MODES**
A. Celma, L. Bijlsma, F.J. López, J.V. Sancho

P-FCH-02 **ADVANTAGES OF PARAFAC DECOMPOSITION IN THE UNEQUIVOCAL IDENTIFICATION AND QUANTIFICATION OF PLASTICIZERS AND BENZOPHENONE MIGRATED FROM FOOD CONTACT MATERIALS BY GC/MS**
L. Rubio, L. Valverde-Som, L.A. Sarabia, M.C. Ortiz

P-FCH-03 **PULSES OF ORGANIC SOLVENT AND THEIR CONSEQUENCES TO ENHANCE ISOCRATIC AND GRADIENT PREDICTIONS**
J.R. Torres-Lapasió, A. Gisbert-Alonso, J.A. Navarro-Huerta, M.C. García-Álvarez-Coque

Industrial processes (IP)

P-IP-01 **CHROMATOGRAPHIC FINGERPRINT OF WOOD PROCESSING INDUSTRY BY-PRODUCTS: EUCALYPTUS, OAK AND CHESTNUT SCREW WATERS**
M. Celeiro, J.P. Lamas, R. Arcas, C. García-Jares, M. Lores

P-IP-02 **SEARCHING BIOACTIVE COMPOUNDS IN WOOD INDUSTRY BY-PRODUCTS: WOODEN CHIPS FROM PINE, WALNUT AND CHERRY**
M. Lores, J.P. Lamas, M. Celeiro, R. Arcas, C. García-Jares

WEDNESDAY OCTOBER 3rd

Poster Session 3:

New developments in instrumentation (NDI) & Omic techniques (OT) & Other applications (OA)

New developments in instrumentation (NDI)

P-NDI-01 **TARGETED AND UNTARGETED SCREENING OF PESTICIDES AND OTHER CONTAMINANTS IN FOOD MATRICES USING A NOVEL HIGH RESOLUTION GC/Q-TOF**
J. Riener, K. Chen, J.J. Rivero

P-NDI-02 **LAB-IN-SYRINGE: A YOUNG AND POWERFUL TECHNIQUE FOR AUTOMATION OF SAMPLE PRETREATMENT**
B. Horstkotte, I.H. Šrámková, H. Sklenářová, P. Solich

P-NDI-03 **UNIQUE GC COLUMN SELECTIVITY FOR TIME AND COST-EFFICIENT SEPARATION OF COMPLEX CIS/ TRANS FATTY ACID METHYL ESTERS IN FOOD**
R. Dhandapani, M.J. Campos Molina

P-NDI-04 **STATIONARY PHASES FOR THE PROCESS SCALE PURIFICATION OF PEPTIDES AND INSULIN ANALOGS**
M. Trass, J. Preston, M. Jacob, G. Krautz, M. McGinley, D. Xing, G. Hodson, N. Filloy, V.R. Thangella

Omic techniques (OT)

P-OT-01 **OIL QUALITY ASAP: DETECTING DEFECTED AND ADULTERATED OILS BY DIRECT MS USING ATMOSPHERIC SOLIDS ANALYSIS PROBE**
C. Sales, L. Lacalle, T. Portolés, J. Beltrán

P-OT-02 **UNTARGETED MULTI-PLATFORM METABOLOMICS APPROACH FOR THE STUDY OF CHILDHOOD CEREBELLAR ATAXIA**
J. Sáiz, G. Nedic Erjavec, C. Barbas, P. Gutiérrez Ríos

P-OT-03 **EVALUATION OF MASS SPECTRAL FINGERPRINTS BY SPME FOLLOWED BY MS FOR CHARACTERIZATION OF HONEY BOTANICAL SOURCE**
J.E. Quintanilla-López, R. Lebrón-Aguilar, M.L. Sanz, A.C. Soria

P-OT-04 **A HUMAN DIETARY INTERVENTION STUDY OF A BIOACTIVE GARLIC SUPPLEMENT BY A FINGERPRINTING METABOLIC APPROACH**
A. Fernández-Ochoa, I. Borrás-Linares, R. Quirantés-Pine, S. Pimentel Moral, A. Baños, E. Guillamón, A. Segura-Carretero

P-OT-05 **A MULTI-PLATFORM METABOLOMIC APPROACH TO SEARCH CHEMICAL MARKERS RELATED TO THE COFFEE ROASTING PROCESS**
R. Pérez-Míguez, E. Sánchez-López, M. Plaza, M.L. Marina, M. Castro-Puyana

P-OT-06 **MULTI LC-MS METHOD APPROACH FOR THE VALIDATION OF POTENTIAL BIOMARKERS FOR THE EARLY DIAGNOSIS OF PARKINSON'S DISEASE**
M. Konjevod, A. Bergareche, P. Amiano, F. Goñi, E. Ardanaz, J.M. Huerta, C. Barbas, J. Sáiz

P-OT-07 **ANALYSIS OF PROTEIN BIOMARKERS BY ON-LINE IMMUNOAFFINITY SOLID-PHASE EXTRACTION CAPILLARY ELECTROPHORESIS-MASS SPECTROMETRY USING Fab' ANTIBODY FRAGMENTS. TRANSTHYRETIN IN FAP-I**
L. Pont, F. Benavente, J. Barbosa, V. Sanz-Nebot

P-OT-08 **METABOLOMICS FINGERPRINTING OF BILE SAMPLES IN A CHOLANGIOCARCINOMA STUDY**
A. López-López, A, López-Gonzálvez, V. Alonso-Herranz, A. Paradela, F.J. Corrales, C. Barbas

P-OT-09 **UNVEILING THE CAPABILITIES OF CE-LIF FOR DETERMINATION OF KEY FREE D-AMINO ACIDS IN HUMAN URINE. APPLICATION TO THE STUDY OF THEIR RELATIONSHIP WITH FERMENTED DAIRY FOOD INTAKE**
M.P. Lorenzo, L. Valiente, A. García

P-OT-10 **STUDY OF THE MINOR FRACTION OF VIRGIN OLIVE OIL BY A MULTI-CLASS GC-MS APPROACH: COMPREHENSIVE QUANTITATIVE CHARACTERIZATION AND VARIETAL DISCRIMINATION POTENTIAL**
L. Olmo-García, J.J. Polari, X. Li, A. Bajoub, A. Fernández-Gutiérrez, S.C. Wang, A. Carrasco-Pancorbo

P-OT-11 **EXPLORING THE CAPABILITY OF LC-MS AND GC-MS MULTI-CLASS METHODS TO DISCRIMINATE OLIVE OILS FROM DIFFERENT GEOGRAPHICAL INDICATIONS AND TO IDENTIFY POTENTIAL ORIGIN MARKERS**
L. Olmo-García, K. Wendt, N. Kessler, A. Bajoub, C.M. Sánchez-Arévalo, A. Fernández-Gutiérrez, C. Baessmann, A. Carrasco-Pancorbo

P-OT-12 **LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY ANALYSIS OF EICOSANOIDS**
C. Díaz-Navarro, P. Mena, A. Martín-Blázquez, O. Genilloud, F. Vicente, J. Pérez-del Palacio

P-OT-13 **NEW POTENTIAL BIOMARKERS OF METASTATIC COLORECTAL CANCER USING AN UNTARGETED LC-HRMS-BASED METABOLOMICS**
A. Martín-Blázquez, C. Díaz-Navarro, C. Jiménez Luna, J.C. Prados, C. Melguizo, O. Genilloud, F. Vicente, O. Caba, J. Pérez-del Palacio

P-OT-14 **INFLIXIMAB AND CETUXIMAB -THERAPEUTIC MONOCLONAL ANTIBODIES-N-GLYCOSILATION ANALYSIS BY UPLC-FLUORESCENCE-QTOF(MS)**
N. Navas, S. Millán, J. Bones

Other applications (OA)

P-OA-01 **PRODUCTION AND COMPREHENSIVE CHARACTERIZATION BY LC×LC-PDA-MS OF AQUEOUS PHASES FROM PYROLYSIS OF DIFFERENT BIOMASSES**
E. Lazzari, E. Bastos Caramão, M. Herrero

P-OA-02 **CHALLENGES IN THE ANALYSIS OF SYNTHETIC DYES IN COSMETICS BY REVERSED PHASE LIQUID CHROMATOGRAPHY COUPLED TO TANDEM MASS SPECTROMETRY**
E. Guerra, J. Pablo Lamas, M. Celeiro, M. Llompart, C. Garcia-Jares

P-OA-03 **STUDY OF PHOTODEGRADATION OF PATENT BLUE V IN ORAL CARE PRODUCTS**
E. Guerra, M. Llompart, C. Garcia-Jares

P-OA-04 **EVALUATION OF THE EFFECT OF AIR-DRYING TEMPERATURE ON PHENOLIC COMPOUNDS OF AVOCADO BY-PRODUCTS BY HPLC-ESI-TOF-MS**
J.G. Figueroa, I. Borrás-Linares, J. Lozano-Sánchez, M.L. Cádiz-Gurrea, A. Segura-Carretero

P-OA-05 **PREPARATION OF A O-[2-(METHACRYLOYLOXY)-ETHYLCARBAMOYL]-10,11-DIHYDROQUINIDINE-SILICA HYBRID MONOLITH FOR THE ENANTIOSEPARATION OF AMINO ACIDS BY NANO-LC**
D. Xu, E. Sánchez-López, Q. Wang, Z. Jiang, M.L. Marina

P-OA-06 **BREATH ANALYSIS FOR THE BIOLOGICAL MONITORING OF CHRONIC EXPOSURE TO VOLATILE ORGANIC COMPOUNDS**
J.M. Sánchez, M. Castellanos

P-OA-07 **PHYTOCHEMICAL PROFILING OF HYDROALCOHOLIC EXTRACT FROM AERIAL PARTS AND ROOTS OF RUTA GRAVEOLENS FROM MORELOS (MEXICO)**
L. Reyes-Vaquero, G. Álvarez-Rivera, E. Ibáñez, P. Vanegas-Espinoza, N. Robledo-Quintos, A. Del Villar-Martínez

P-OA-08 **PYROLYSIS-COMPOUND-SPECIFIC ISOTOPE ANALYSIS (PY-CSIA δ2H) OF EXTRA VIRGIN OLIVE OILS FROM THE MEDITERRANEAN BASIN**
N.T. Jiménez-Morillo, M.J. Cabrita, C.B. Dias, F.J. González-Vila, J.A. González-Pérez

P-OA-09 **DETERMINATION OF LIMONENE IN RECYCLED HDPE PELLETS**
José Mª Sangenís, Ashleigh Mellor

Poster Session 4:

Food analysis (FA)

P-FA-01 **ANALYSIS OF PESTICIDES IN TEA LEAF AND HONEY USING THE NEW INTUVO PLATFORM COUPLED TO GC MS/MS**
J. Riener, J. Westland, J.J. Rivero

P-FA-02 **ANALYSIS OF HALOANISOLES AND TRIOCTENON IN WINE USING SPME COUPLED GAS CHROMATOGRAPHY AND TIME-OF-FLIGHT MASS SPECTROMETER**
J. Lluch

P-FA-03 **CHARACTERIZATION AND CLASSIFICATION OF ARABICA AND ROBUSTA COFFEES BY LIQUID CHROMATOGRAPHY, MASS SPECTROMETRY AND CHEMOMETRIC METHODS**
N. Núñez, X. Collado, O. Núñez, J. Saurina

P-FA-04 **DETERMINATION OF POLYPHENOLS IN PAPRIKA (*CAPSICUM ANNUUM L.*) BY UHPLC-ESI-MS/MS. PROTECTED DESIGNATION OF ORIGIN CLASSIFICATION BY PARTIAL LEAST SQUARES DISCRIMINANT ANALYSIS**
G. Campmajó, S. Barbosa, O. Núñez, J. Saurina, L. Puignou

P-FA-05 **DETERMINANTION OF ETHOXYQUIN AND ITS DIMER IN PEAR SKIN AND SALMON SAMPLES BY LIQUID CHROMATOGRAPHY WITH ELECTROCHEMICAL DETECTION**
R. Rodríguez-Gómez, M. Vandeput, A. Zafra-Gómez, J.M. Kauffmann

P-FA-06 **DEVELOPMENT AND VALIDATION OF LC-MS/MS METHOD FOR THE CHARACTERIZATION OF REFERENCE MATERIALS FOR PESTICIDES RESIDUES ANALYSIS IN FRUITS: A METROLOGICAL APPROACH**
M.A. Paredes Rozo, J. Arturo Guerrero, S. González-Mónico

P-FA-07 **PLASTICIZERS IN CAPSULES OF DIETARY SUPPLEMENTS FOR OVERWEIGHT CONTROL**
M.A. Fernández, S. Garrido, E. Nogales, L. Ramos, B. Gómara

P-FA-08 **MONITORIZATION OF PHENOLIC COMPOSITION OF MANGO PEEL (*Mangifera indica*) by HPLC-DAD-q-TOF-MS DURING FIVE RIPENING STAGES**
M.E. Alañón, A.M. Gómez-Caravaca, D. Arráez-Román, A. Segura-Carretero

P-FA-09 **EMULSION TECHNOLOGY FOR THE DEVELOPMENT OF FUNCTIONAL OILS**
S. Pimentel-Moral, C. Rodríguez-Pérez, A. Fernández-Ochoa, D. Arráez-Román, A. Martínez-Férez, A. Segura-Carretero

P-FA-10 **QUALITATIVE AND QUANTITATIVE DIFFERENCES ON THE PHENOLIC PROFILE OF PLE LEAVES EXTRACTS OBTAINED FROM FOUR *MORUS ALBA* VARIETIES**
F.J. Leyva-Jiménez, J. Lozano-Sanchez, I. Borras-Linares, M.L. Cadiz-Gurrea, J. Gálvez-Peralta, D. Arraez-Román, A. Segura-Carretero

P-FA-11 **RECOVERING OF ANTI-INFLAMATORY AND ANTI-OBESOGENIC COMPOUND FROM *LIPPIA CITRIODORA* LEAVES BY SUB-CRITICAL FLUIDS EXTRACTION**
F.J. Leyva-Jiménez, J. Lozano-Sanchez, I. Borras-Linares, M.L. Cadiz-Gurrea, D. Arraez-Román, A. Segura-Carretero

P-FA-12 **DOWNSTREAM GREEN PROCESSES FOR RECOVERY OF BIOACTIVE COMPOUNDS FROM *Porphyridium cruentum*: TOWARDS A MICROALGAL BIOREFINERY**
R. Gallego, M. Martínez, E. Ibáñez, M. Herrero

P-FA-13 **USE OF COMBINED ANALYTICAL TECHNIQUES TO PREVENT LABELLING FRAUD OF IBERIAN HAM**
A. Martín-Gómez, N. Arroyo-Manzanares, A.I. López-Lorente, V. Rodríguez-Estévez, L. Arce

P-FA-14 **HS-GC-IMS AS A POWERFUL ANALYTICAL TOOL TO CLASSIFY OLIVE OIL: EXPLORING DATA TREATMENT AND CHARACTERISTICS OF TWO DEVICES**
N. Jurado-Campos, M.M. Contreras, N. Arroyo-Manzanares, L. Arce

P-FA-15 **IS GC-IMS A SUITABLE INSTRUMENT FOR ROUTINE ANALYSIS?**
A. Martín-Gómez, N. Jurado-Campos, M.C. Alcudia-León, N. Arroyo-Manzanares, L. Arce

P-FA-16 **TOWARD THE VALORIZATION OF CURUBA (*Passiflora mollissima* (Kunth) L. H. Bailey) SEEDS: SUSTAINABLE EXTRACTION AND CHEMICAL CHARACTERIZATION**
D. Ballesteros-Vivas, G. Álvarez-Rivera, E. Ibánez, F. Parada-Alfonso, A. Cifuentes

P-FA-17 **HPAEC-PAD ANALYSIS OF FERMENTATION SELECTIVITY OF NEWLY SYNTHESIZED OLIGOSACCHARIDES BY HUMAN-DERIVED BIFIDOBACTERIAL SPECIES**
L. Ruiz-Aceituno, M. Esteban-Torres, V. Ambrogi, K. James, D. van Sinderen, F.J. Moreno

P-FA-18 **BEHAVIOR OF PECTIN DURING IN VITRO GASTROINTESTINAL DIGESTION AND EFFECT ON HUMAN COLONIC MICROBIOTA**
A. Ferreira-Lazarte, I. Gil, C. Cueva, F.J. Moreno, M. Villamiel

P-FA-19 **DETERMINATION OF SELECTED PHARMACEUTICALS IN LETTUCE CROPS BY HRMS X500R Q-TOF**
M. García-Vara, N. Montemurro, A. Juan, S. Pérez

P-FA-20 **STUDY OF PEPTIDE COMPOSITION IN COFFEE SILVERSKIN PROTEIN HYDROLYSATES SUBMITTED TO DIFFERENT ROASTING PROCESSES BY LC-ESI-QTO**
R. Pérez-Míguez, M.L. Marina, M. Castro-Puyana

P-FA-21 **MALDI-TOF MS ANALYSIS OF PROCYANIDINS DERIVED FROM *VITIS VINIFERA L.* SEEDS DISAGGREGATED BY ULTRASOUND**
A. Muñoz-Labrador, M. Prodanov, F.J. Moreno, M. Villamiel

P-FA-22 **CHROMATOGRAPHIC CHARACTERIZATION OF PECTINS EXTRACTED FROM ARTICHOKE BY-PRODUCTS USING ULTRASOUNDS**
C. Sabater, N. Corzo, A. Olano, A. Montilla

P-FA-23 **IDENTIFICATION OF BIOACTIVE PEPTIDES AND POLYPHENOLS IN HIGHLY BIOACTIVE EXTRACTS OBTAINED FROM POMEGRANATE (*PUNICA GRANATUM L.*) PEEL BY RP-HPLC-ESI-Q-TOF**
E. Hernández-Corroto, M.L. Marina, M.C. García

P-FA-24 **ANTIOXIDANT PHENOLIC PROFILE CHARACTERIZATION OF PEEL FROM DIFFERENT PASSIFLORA SPECIES BY HPLC-DAD-QTOF/MS**
G. Domínguez-Rodríguez, M. Plaza, M.C. García, M.L. Marina

P-FA-25 **A CAPILLARY-LC-IT-MS/MS METHODOLOGY FOR THE QUANTITATION OF FOUR ACE-INHIBITORY PEPTIDES IN PRUNUS SEED HYDROLYSATES**
E. González-García, M.C. García, M.L. Marina

P-FA-26 **HEADSPACE SOLID-PHASE MICROEXTRACTION GAS CHROMATOGRAPHY-MASS SPECTROMETRY FOR THE DETERMINATION OF SEMI-VOLATILE FLUORINATED COMPOUNDS IN MICROWAVE POPCORN BAGS**
A. Contreras-Llin, J.F. Ayala-Cabrera, E. Moyano, F.J. Santos

P-FA-27 **DEVELOPMENT OF DISPERSIVE SOLID PHASE EXTRACTION METHOD FOR THE ANALYSIS OF PHOTOINITIATORS IN FATTY FOOD BY UHPLC-MS/MS**
N. Medina, R. Seró, E. Moyano

P-FA-28 **COMBINED (d)SPE-QuEChERS EXTRACTION OF MYCOTOXINS IN UNIFEED AND ANALYSIS BY HPLC-HRMS**
R. Facorro, M. Llompart, T. Dagnac

P-FA-29 **DETERMINATION OF *FUSARIUM* EMERGING MYCOTOXINS IN VEGETABLES MILKS BY UHPLC-MS/MS**
L. Gámiz-Gracia, N. Arroyo-Manzanares, A.M. Hamed, A.M. García-Campaña

P-FA-30 **DETERMINATION OF MULTI-MYCOTOXIN OCCURRENCE IN FOODSTUFF FROM ALGERIA BY ULTRA HIGH PERFORMANCE LIQUID CHROMATOGRAPHY COUPLED TO TRIPLE QUADRUPOLE MASS SPECTROMETRY (UHPLC-MS-MS)**
C. Khelifa Mahdjoubi, N. Arroyo-Manzanares, N. Hamini, A.M. García-Campaña, L. Gámiz-Gracia

P-FA-31 **A PROPOSAL FOR ON-LINE DERIVATIZATION OF AFLATOXINS IN UHPLC WITH FLUORESCENCE DETECTION FOR THEIR DETERMINATION IN RICE SAMPLES**
N. Arroyo-Manzanares, J.F. Huertas-Pérez, A.M. García-Campaña, L. Gámiz-Gracia

P-FA-32 **APPLICATION OF CAPILLARY LIQUID CHROMATOGRAPHY TO THE ANALYSIS OF 5-NITROMIDAZOLES IN AQUACULTURE PRODUCTS USING MOLECULARLY IMPRINTED SOLID PHASE EXTRACTION AS SAMPLE TREATMENT**
M. Hernández-Mesa, D. Moreno-González, C. Cruces-Blanco, A.M. García-Campaña

P-FA-33 **DIFFERENT CHEMOMETRICS APPROACHES FOR CLASSIFICATION OF VIRGIN OLIVE OILS USING GAS CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY**
M. García-Nicolás, N. Arroyo-Manzanares, L. Arce, M. Hernández-Córdoba, P. Viñas

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C. Carrero-Carralero, S. Rivas, S. Rodríguez-Sánchez, L. Ramos, A.C. Soria, M.L. Sanz

P-FA-40 **A COMPREHENSIVE CHARACTERIZATION OF RASPBERRY KETONE SUPPLEMENTS FOR OVERWEIGHT CONTROL**
S. Rodríguez-Sánchez, A. Mena, M.L. Sanz, A.C. Soria

P-FA-41 **UNRAVELLING TROPANE ALKALOIDS DEGRADATION FROM BAKED BUCKWHEAT SAMPLES**
J. Marín-Sáez, R. Romero-González, A. Garrido Frenich

P-FA-42 **DETERMINATION OF TRANS-ANETHOLE AND MYRISTICIN IN INFUSION PRODUCTS BY ULTRASOUND EXTRACTION AND GAS CHROMATOGRAPHY-MASS SPECTROMETRY**
A. Rivera-Pérez, R. López-Ruiz, A. Garrido Frenich

PL1

PUSHING THE LIMITS OF SEPARATIONS: HIGH SPEED AND HIGH PRESSURE

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In this talk we provide an overview of recent advances in fast separations, with a focus on proteins by electrophoresis, and ultra high pressure LC.

Microchip electrophoresis enables high speed separations on small samples which opens new possibilities for chemical analysis. Such systems are particularly attractive for protein assays. We have explored new ways of using microchip electrophoresis for protein analysis related to high-throughput screening (HTS) and western blotting. The high speed of electrophoresis allows intact non-covalent complexes to be separated and detected. This capability has been extensively used for immunoassay and aptamer assay. We have recently demonstrated that we can separate protein-protein complexes involved in intracellular signaling to generate quantitative information on binding and selectivity. For proteins that dissociate, we have investigated protein-cross-linking capillary electrophoresis (PXCE). Assays in a few seconds are possible by both approaches. We have also demonstrated fast (< 1 s) separations of substrates and products from enzymes allowing rapid enzyme assays. The high speed of the assays suggests they could be used in HTS for drug discovery. To achieve this, we have developed a droplet microfluidic system that allows discrete samples to be rapidly loaded in sequence onto a chip for injection and separation. Using this method over 1000 injections have been achieved in 17 min. Preliminary results suggest the method is stable enough for HTS opening the door to robust HTS of protein-protein interactions and enzyme activity. The droplet system has also been interfaced to mass spectrometry for assays at rates up to 5/s. A third approach that we have investigated is a microchip western blot. Western blotting is one of the most widely used protein assays and the lack of a miniaturized counterpart has likely held back the use of microfluidics in routine biochemistry. We have interfaced chip separations to blotting membranes for rapid westerns. Potential for multi-protein analysis is greatly enhanced by this method.

Another extreme that we have explored is high pressure for LC. It is well-known that smaller particles and longer columns, which provide higher resolution, require higher pressure for flow in LC. As a result, advances in LC systems have been made that allow operation up to 15,000 psi. We have experimented with systems that operate up to 40,000 psi. We demonstrate that the higher resolving power allows improved chemical information content for complex lipid samples.

PL2

ANALYSIS OF COMPLEX MIXTURES BY COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY-MASS SPECTROMETRY: NON-ORIENTATED STUDIES

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Despite the high-resolution power offered by gas chromatography, and the improved identification capabilities derived from its hyphenation with a detection system able to provide structural information, such a mass spectrometer (GC-MS), the analysis of residual compounds in complex extracts is often hampered by coelution either with co-extracted matrix components or with other structurally-related compounds remaining in the extract. This type of problem is more likely to occur when the goal of the analysis is the non-targeted analysis (i.e., comprehensive characterization) of the investigated sample due to the simplified sample treatment procedures typically adopted for such a type of determination. In these cases, appropriate and reliable identification and/or quantification of the analytes present in the extracts require enhanced separation and identification capabilities and, therefore, the use of a technique like comprehensive two-dimensional gas chromatography couple to time-of-flight mass spectrometry (GC×GC−ToF MS) is particularly advisable.

In this presentation, after a brief description of the GC×GC−ToF MS basis, the potential of the technique for the exhaustive characterization of the (semi-)volatile organic compounds present in complex extracts related to food and environmental analysis will be illustrated through selected application studies.

PL3

THOUSANDS OF SEPARATED SIGNALS IN A FOUR-DIMENSIONAL SEPARATION APPROACH: HOW CAN WE MANAGE THE DATA?

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Complex samples in the field of metabolomics, lipidomics, environmental and food analysis are often analyzed by liquid chromatography coupled to a high-resolution mass spectrometer (HRMS). But there are three major problems in the analysis of complex samples with LC-MS, which make an analysis very difficult. At first, with a high-resolution mass spectrometer (HRMS) a fantastic mass resolution with high accurate mass is possible, which allow us to calculate a sum formula. Unfortunately, it is not possible to construct the structure only with the sum formula and usually more as one, often tens or sometimes hundreds of compounds show the same sum formula, which do not allow an identification of the analytes in the sample. Secondly, the separation power of a one-dimensional LC (1D-LC) is often not sufficient for a baseline separation of complex samples. This leads to coelutions, which means that several, often tens or more, compounds are in the ion source at the same time. Because of this coelution ion suppression takes place – especially with an electrospray ion source (ESI) -, which makes a quantitative analysis more difficult. Furthermore, the coelution leads to mixed MS spectra, increasing also the problems in spectra interpretation. The third problem is that the method development for complex samples is very difficult and takes time.

Here, we present a two-dimensional chromatography method (LC+LC [1] and GC+GC [2] coupled to an ion mobility-high resolution mass spectrometer. This approach works as a continuous multiheart-cutting system, using a long modulation time of four minutes (LC+LC) or 20 s (GC+GC), which allows the complete transfer of most of the first dimension peaks to the second dimension column without fractionation, in comparison to comprehensive two-dimensional chromatography. Hence, it is possible to look at the data from a 2D analysis in a simple 1D chromatogram, which simplifies the data handling even when IMS as a third and MS as a fourth dimension are introduced. The analysis of various complex samples with LC+LC or GC+GC-IM-qTOF-MS shows the separation power of this four dimensional separation method with an outstanding peak capacity of more than 8000. These analyses show in most cases pure mass spectra, which is an indicator for base line separation. Furthermore, the advantage of ion mobility for characterizing unknown compounds by their collision cross section (CCS) and accurate mass in a non-target approach is shown for different matrices.

In addition, we will show the challenges in data management of such big data files in a multi-dimensional separation approach.

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PL4

NEW INSIGHTS INTO SEPARATION TECHNIQUES FOR ENDOGENOUS METABOLOMIC PROFILING

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Metabolomic sciences aim at the study of low molecular weight molecules in different biological matrices. LC-HRMS approaches are often used in the context of untargeted acquisition workflows. Taking into account the fact that human metabolites span across a wide range of polarity values, RPLC is the option of choice for the mid- to apolar metabolites and HILIC for the polar or ionized compounds. Although the application of all the available LC-HRMS techniques will always provide the most comprehensive set of chemical information from the specimens, the simultaneous deployment of numerous analytical methods will be rarely possible due to the limitations in terms of time, human and material resources. Therefore, guessing which combination of LC and ionization techniques is the most efficient one becomes a pivotal question to optimize the analytical investment.

Another important aspect in the investigation of the metabolic content is the annotation of the detected metabolites. This is mandatory to obtain an optimal interpretation of the biological information present in the studied systems. To make possible the annotation of features, databases gathering different physicochemical properties of standards are often measured in-house to achieve enough reliability along the identification process. To evaluate the performance of different LC and MS methods to detect and identify endogenous metabolites by comparison to reference standards, a chemical library containing above 800 metabolites was investigated in our laboratory with generic HILIC and RPLC methods hyphenated to MS in positive and negative acquisition modes.

Herein, we introduce an ad-hoc developed scoring process allowing to integrate different measurable parameters of the analytical response obtained for each analyte on each technique. Such scores allowed to evaluate and rank the performance of the different LC-HRMS methods according to their suitability to analyze each compound. By applying this strategy, it was possible not only to find the optimal combination of LC methods to maximize the output-to-investment ratio of the analyses, but also to select univocally annotated features for further data treatment.

This approach was applied in the context of an *in vitro* human astrocyte model to investigate metabolic changes related to neuroinflammation. Neural cells were exposed to different neuroinflammatory inducers for different time spans and cell contents were analyzed. Variables contribution decomposition allowed to characterize the relative importance of every metabolite in the global model but also to address the specific variability that could be considered when interpreting one effect.

PL5

CURRENT TRENDS IN SAMPLE TREATMENT FOR ENVIRONMENTAL ANALYSIS

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Nowadays, tons of chemicals from industrial, agricultural and household applications enter the environment and are distributed along all compartments, having impact on ecosystems, biodiversity and, in the last term, on human health. There is strong evidence that chemical exposure has been associated with adverse health effects. Some environmental pollutants are demonstrated endocrine disruptors, carcinogens or mutagens, such as pesticides, plastic additives, and personal care products; while others are suspected to present those behaviors. Therefore, the European Union has established environmental legislations to control chemical pollution, preserving the ecosystems and protecting human health.

Environmental samples comprise a wide variety of complex matrices, frequently with low concentrations of analytes and many interferences. Consequently, sample treatment is a critical step and the main source of uncertainty in the analysis of environmental samples. Moreover, and depending on the selected analytical strategy, several steps should be carried out such as extraction, clean-up, evaporation, derivatization and determination. The development of reliable methods for the determination of pollutants at low concentrations (trace/ultratrace levels) is a current analytical challenge, mainly for environmental control laboratories to ensure compliance with the limit values set by the environmental regulations.

Classic extraction techniques are characterized by larger analysis time, several tedious steps and the higher use of toxic reagents and waste generation. However, their low cost, the availability in laboratory routine analysis and their incorporation in some standardized protocols support the employment of these extraction techniques. New trends in sample treatment includes alternative techniques based on less time and solvent consumption, lower sample handling, miniaturization and automation. Some of these techniques are coupled to gas/liquid chromatography-mass spectrometry allowing the extraction, clean-up and determination of target analytes in one step, simplifying the sampling handling and reducing the analysis time [1-2]. Applications of miniaturized and microextraction techniques to selected analytes and different environmental matrices will be presented.

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PL6

ADVANCED ANALYTICAL STRATEGIES IN THE FIELD OF BIOACTIVE INGREDIENTS

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This presentation summarizes the experience of the Group "Bioactive Ingredients" (AGR 274) in the last years about the use of advanced separative techniques coupled to high resolution mass spectrometry for the characterization of bioactive compounds, especially phenolic compounds, and metabolomic studies from different vegetal plant such as *Rosmarinus officinalis*, *Lippia citriodora*, *Olea europaea* or *Hibiscus sabdariffa*.

Throughout history, a large number of plants have been used in folk medicine for the prevention and treatment of various diseases in both humans and animals. The ability of some plant-based foods to reduce the risk of certain diseases has been associated, at least in part, with the secondary metabolites or phytochemicals present in these plants, which have been shown to exert a wide range of biological activities. That is why in recent years a large part of the research in the field of nutraceuticals has focused on these phytochemicals, studying in detail both composition and bioactivity of various plant species traditionally used as medicinal plants [1-4].However, the characterization of the bioactive compounds requires the use of a methodology well established based on a previous sample treatment, the use of analytical separation techniques (especially the LC separation technique) coupled to different detection systems (UV-Vis spectroscopy, TOF-MS, QTOF-MS, and UHR-Qq-TOF-MS) and the support of different databases. If the characterization is a challenge for the Analytical Chemistry, the studies of adsorption, pharmacokinetic and metabolomics of these bioactive compounds can supposed to develop strategies more precise and sophisticated based in advanced analytical tools in order to get interesting results to demonstrate the bioactivity of these compounds against different pathologies.

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O1

POTENTIAL OF ION MOBILITY-MASS SPECTROMETRY FOR BOTH TARGETED AND UNTARGETED CHARACTERISATION OF PHASE II STEROID METABOLITES IN URINE

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In recent years, the commercialization of hybrid ion mobility-mass spectrometers and their integration in traditional liquid chromatography-mass spectrometry (LC-MS) workflows have opened new opportunities for extending the current boundaries of targeted and untargeted analyses [1]. Ion mobility spectrometry (IMS) provides an additional separation dimension that improves method selectivity and sensitivity by the separation of isobaric and isomeric compounds and the isolation of the analytes of interest from the background noise. Furthermore, IMS allows measuring the averaged collision cross section (CCS, Ω) of molecules, resulting in complementary information to retention time and mass spectra. As a consequence, compounds can be identified with more confidence, either in targeted or untargeted approaches [2]. Within this framework, we have recently reported the first CCS database for the identification of 300 steroids (i.e., endogenous, including phase I and phase II metabolites, and exogenous synthetic compounds), considering the relevance of these compounds in the fields of food safety and doping control, as well as in metabolomics studies [3]. This database covers the CCS of 127 androgens, 84 estrogens, 50 corticosteroids, and 39 progestagens. In the present work, the influence of the matrix (i.e. bovine urine) on the CCS values of phase II steroid metabolites (i.e. steroid glucuronides and sulfates, n = 25) was evaluated for increased confidence on the subsequent application of the database. Urine samples were diluted 10-fold with aqueous formic acid (0.1%, v/v) prior analysis. In general, deviations lower than 1% have been observed between the CCS values from the database and the CCSs measured in urine samples over three months. Only a slight influence of adult bovine urine matrix on the CCS of certain steroid metabolites could be observed in comparison with calve urine matrix, which is a less complex sample. Interestingly, it has been observed that signal-to-noise (S/N) ratio can be improved at least 2 or 3-fold when IMS is combined with LC-MS. Finally, as a proof of concept application, boldenone 17α-glucuronide has been identified as one of the main metabolites resulted from boldione administration to calves based on CCS measurements.

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O2

LC-MS/MS QUANTITATION OF STEROID SULFATE METABOLITES TO EVALUATE ITS POTENTIAL AS MARKERS OF TESTOSTERONE ADMINISTRATION

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A method based on liquid chromatography-tandem mass spectrometry for the direct quantitation of endogenous steroid sulfates has been developed to evaluate these metabolites as potential biomarkers to detect the misuse of endogenous androgenic anabolic steroids in sports. A mixed-mode solid-phase extraction using WAX cartridges was optimized to eliminate the glucuronide fraction and other interferences in the washing step thus obtaining only the sulfate fraction. Several mobile phase composition and chromatographic columns were tested to achieve an adequate separation between compounds, particularly between isomers (sulfates of androsterone/eticholanolone, epiandrosterone/dihydrotestosterone). The MS behavior of the sulfates were studied in order to obtain the most specific and selective transitions. The method was validated for eleven endogenous steroid sulfates and satisfactory results were obtained for all compounds. Relative standard deviation of intra- and inter-day precision was better than 16.2%. Limits of quantitation ranged between 0.5 and 2 ng/mL. Extraction recoveries were higher than 90% for all compounds. Matrix effect ranged from 90-110%. Samples were found to be stable after two freeze/thaw cycles. Moreover, the acquisition of generic transitions in SRM mode allowed the identification of three additional androstanediol sulfates.

The method was applied to urine samples collected from five Caucasian volunteers after testosterone oral administration in order to evaluate sulfate metabolites as markers of its misuse. Principal component analysis was used to study ratios between all analytes in order to obtain the markers that are most significant in the separation between pre- and post-administration samples.

Detection times for sulfates and significant ratios were evaluated. For oral administration promising results were obtained with some sulfates (such as epiandrosterone sulfate) and ratios (epiandrosterone sulfate/epitestosterone sulfate or androstandiol 1 sulfate/dehydroandrosterone sulfate) that are detected up to 144 h, significant higher compared to those obtained with testosterone/epitestosterone ratio. Thus, sulfates metabolites could be used as complement markers of steroid profile.

O3

CHALLENGES OF MINIATURIZING TRIPLE-QUADRUPOLE MASS SPECTROMETERS WHILE MAINTAINING HIGH PERFORMANCE

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This year we celebrate the fortieth anniversary of the introduction of the triple quadrupole mass spectrometer (TQ). At that time, Professor Christie Enke and his graduate student Rick Yost, were searching for a computerized alternative to traditional chromatography that would facilitate separation and identification of chemical species. A rather serendipitous encounter with Professor James Morrison of La Trobe University in Melbourne, Australia led to enlightening discussions and eventual collaboration that gave birth to the "Selected Ion Fragmentation Tandem Mass Spectrometer (SIFT)" [1].

Since its initial introduction, the TQ has been a staple for varied qualitative and quantitative analyses [2,3,4]. However, over the last decade qualitative analyses have largely migrated to higher-resolution alternatives [5], while the TQ remains as the instrument of choice for quantitative analyses [6]. This in part is due to the high degree of specificity provided by the "Multiple Reaction Monitoring" Mode (MRM) of operation where a specific parent/product ion transition are observed during the measurement. With emerging needs for quantitative assessments in the fields of food safety, environmental pollutants, clinical research, pharmaceutical discovery and development, and toxicology amongst others, the TQ instrument has become a focal component of the modern analytical laboratory [7]. Although major improvements have been made in ion source design, ion optics, vacuum systems, quadrupole design, detectors and overall ion transmission efficiencies, the size of these instruments has remained largely unchanged [8]. Here, we discuss the challenges of encountered when significantly reducing the form-factor of a TQ instrument, while maintaining performance characteristics of traditionally larger systems. Specifically, we will discuss revamp of the electronics and mechanical assemblies, along with improvements to the ion optics and vacuum systems to maintain system performance. Lastly, we will discuss how these ramifications are geared towards enabling use of the technology by an ever-changing user base.

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O4

TARGET AND SUSPECT ANALYTICAL STRATEGIES FOR THE EVALUATION OF CONTAMINANTS OF EMERGING CONCERN IN AGRICULTURAL SOILS AND CROPS IRRIGATED WITH RECLAIMED WASTEWATER: TWO YEARS MONITORING

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Nowadays, water scarcity for agriculture purposes has become one of the main problems worldwide due to the climate change and raising population. In Mediterranean countries, where low rainfall is unevenly distributed over the year and water resources are limited, reuse of reclaimed wastewater (RWW) for crop irrigation is essential to deal with water shortages. This practice reduces fresh water withdrawals and contributes to an efficient water usage.

Nevertheless, the inefficient removal of contaminants of emerging concern (CECs) in wastewater treatment plants (WWTPs) leads to the spread of CECs in the soil-plant system, with long-term consequences not yet fully evaluated, for consumers and environment. These CECs are released in agricultural fields after repeated RWW irrigation occurrences, being able to accumulate in soils and translocate to crops intended for human consumption. Their behavior and persistence depend on their different physical-chemical properties, adsorption, conjugation form and charge in the soil-compound system, but also on soil characteristics, type of crop and agricultural practices.

Therefore, multiresidue analytical strategies are required to improve current knowledge on the fate of CECs under real agricultural conditions. In this work, a combined target and suspect strategy have been developed for the comprehensive analysis of CECs in real field tomato crops irrigated with RWW. Soils and tomato fruit and leaves were investigated. Target analysis included 73 CECs, which were evaluated in the three matrices by using a QuEChERS-based extraction method followed by liquid chromatography coupled to quadrupole-linear ion trap mass spectrometry (LC-QqLIT-MS/MS) analysis. Furthermore, a suspect workflow for the screening of a list of 1300 potential contaminants using LC coupled to quadrupole-time-of-flight MS (LC-QTOF-MS/MS) was applied. The results demonstrated the occurrence of 11 CECs in soils (0.1 to 17 ng g-1, d.w.), 11 in leaves (0.2 to 32 ng g-1, w.w.) and 7 in tomato, although at remarkable lower concentration levels (0.01 to 0.86 ng g-1, w.w.) in the last case. The suspect analysis leaded to the confirmation of up to 28 CECs from the list of candidates. Both strategies revealed the presence of 11 not previously reported compounds.

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O5

SIMULTANEOUS ANALYSIS OF GLYPHOSATE AND ITS DERIVATIVE, (AMINOMETHYL)PHOSPONIC ACID, IN HUMAN URINE BY GC-MS-MS AT LOW PPB LEVELS

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Glyphosate (N-(phosphonomethyl)glycine)) (GLY) is the active ingredient of the broad-spectrum herbicide “Roundup”. Since its commercial introduction in 1974 has rapidly become the most extensively used herbicide worldwide. More than 746 million kg of active ingredient were used for global agriculture in 2014 [1]. The International Agency for Research on Cancer classified GLY as “probable carcinogenic for humans" (category 2A) [2] and several studies indicate a relation between GLY and genotoxic, hormonal, enzymatic type, reproductive, and neurological health risks to humans. The main degradation product of GLY is aminomethylphosphonic acid (AMPA). Despite GLY and AMPA sorb strongly to soils, these compounds have been found in environmental compartments, foodstuff and human samples. The major exposure pathway for GLY in the general population is food that contains residues of the herbicide and is excreted from body via feces and urine. Accordingly, urine is an adequate noninvasive matrix to investigate human exposure.

Although there are some analytical methods for the determination of GLY and AMPA, many developed methodologies reported insufficient limits of detection for the environmental or human biomonitoring studies. The analysis of these substances, particularly in polar matrices, is especially difficult due to their amphoteric character, low volatility, high aqueous solubility and the absence of a UV chromophore group in the molecule. In the present study, a highly selective and sensitive gas chromatography coupled to tandem mass spectrometry (GC-MS-MS) method for the simultaneous analysis of GLY and AMPA in human urine has been developed. It involves previous esterification and acetylation of the acid and amine groups with trifluoroacetic anhydride (TFAA) and trifluoroethanol (TFE) to obtain less polar and more volatile compounds amenable for gas chromatography analysis. Several aspects have been optimized to achieve the low limits of detection (0.10 ng mL^{-1} for GLY and 0.30 ng mL^{-1} for AMPA) required for their determination in urine samples. They include sample clean-up, derivatization conditions, compound stability, solvent for GC injection, MS ionization mode, and MS-MS parameters as well as the quantification methodology. Isotopically labelled analogs of GLY and AMPA were used as standards for quantitation by isotope dilution. The described methodology is simple and fast, avoiding complex extraction and clean up procedures, which usually compromise the method efficiency. Once validated, this method was applied to determination of GLY and its derivate in human urine from people living close to agricultural area.

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O6

STRATEGIES FOR TARGET AND SUSPECT SCREENING OF PHARMACEUTICALS IN WASTEWATER EFFLUENTS USING SWATH APPROACH WITH X500R QTOF

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A considerable number of studies have reported the presence of pharmaceuticals and related compounds in wastewater effluent samples from wastewater treatment plants [1-3]. In fact, current wastewater treatment plants (WWTPs) are not specifically designed to eliminate these pollutants. Thus, many of them are able to pass through wastewater treatment processes into receiving water bodies (rivers, lakes, and sea), posing not only a risk to aquatic organisms but also impacting the quality of food crops and drinking water through irrigation and groundwater recharge. As a consequence, the analysis of wastewater effluent samples is of huge importance to understand the impact of these contaminants on human, aquatic and plant life.

Recently, high resolution and accurate mass spectrometry LC-HRMS/MS systems have been increasingly used for the screening of environmental samples. Indeed, high resolution hybrid mass systems, such as Time-of-Flight (TOF) spectrometers, have facilitated greater reliability in screening applications, providing structural information for many pharmaceuticals and transformation products, in surface water and wastewater.

In this context, the new SCIEX X500R QTOF is the latest TripleTOF, a compact hybrid quadrupole time-of-flight mass spectrometer combining advantages of TOF and QqQ systems with accurate mass. Designed for routine use, the X500R is a versatile tool able to work in different configurations, providing the ability to perform target analysis (using reference standards) and non-target screening on a routine basis. One of the acquisition methods that can be efficiently performed on the new X500R is MS/MS^{All} with SWATH acquisition. SWATH technology is a non-target acquisition method providing MS/MS information of all precursor ions across a specified mass range in pre-divided mass windows allowing more selective MS/MS data collection compared to other MS/MSAll techniques.

In this study we investigated the use of MS/MS^{All} with SWATH acquisition for identification and quantification of pharmaceuticals and personal care products in wastewater effluent samples. We aimed to perform a simultaneous screening and quantitative method using the new SCIEX X500R LC-MS/MS system with SCIEX OS 1.4 software. We also evaluated the detection sensitivity of MS/MS information data for a confident identification through a MS/MS library match against the new HR-MS/MS spectral library 2.0, a new All-in-one library, including the more relevant compounds as pesticides, antibiotics, mycotoxins, veterinary drugs, pharmaceuticals, and drugs of abuse of the NIST library 2017 for a total of almost 14000 compounds.

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O7

ENATIOSELECTIVE DETERMINATION OF CATHINONES IN URINE BY HIGH PRESSURE IN-LINE SPE-CE

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In recent years, synthetic cathinones, a type of drugs of abuse which can be easily found as "bath salts" in internet, have experienced an increase in consumption [1]. Capillary electrophoresis (CE) has proven to be a suitable technique for the determination of cathinones in biological and environmental samples [2], since it has numerous advantages such as high separation efficiency or low cost. In the other hand, the poor sensitivity of the CE-DAD can be solved by the in-line coupling with solid-phase extraction (in-line SPE-CE), since it is possible to introduce large volume of sample, achieving high preconcentration factors [3].

In this study an analytical method for the determination of a group of cathinones (*R,S*-MDPV, *R,S*-mephedrone and *R,S*-4-methylphedrine) in urine by in-line SPE-CE, using a sample pretreatment based on LLE has been developed. The separation electrolyte consists of 70 mM NaH_2PO_4 (pH 2.5) containing 5 mM β-CD and 8 mM hydroxypropyl β-CD in order to achieve an enantioselective separation of the compounds.

To achieve the low concentration levels at which cathinones are usually present in biological samples, in-line SPE-CE was used. The initial conditions used were the previously optimized by Baciu *et al*. [2]. Despite the good results obtained, an inconvenient of that procedure is the large sample loading time needed to achieve low LODs. In order to reduce the sample loading time, which is associated to a large analysis time, while keeping low LODs, different strategies have been considered. In particular some related to the design of the SPE device (length and internal diameter) and also we have evaluated the effect of introducing the sample at high pressure. An increase of injection pressure implies a reduction of the injection time, keeping the injection volume. The optimum conditions for the sample loading step were 3 bar of pressure and 20 minutes (which is below the usual 30 to 60 minutes). Different lengths and internal diameters of the SPE device were evaluated in order to study if by increasing the dimensions of the preconcentrator the amount of analytes retained in the sorbent suffers an increase. Optimum conditions have been achieved with a preconcentrator of 2 mm length, 150 µm internal diameter and filled with 60 µm Oasis HLB sorbent particles. By using these conditions it has been possible to reach low LODs.

The developed method provided good linearity and LODs between 3 and 8 ng/mL in urine samples, hence below the usual concentrations found of these drugs in urine, with satisfactory precision, in both intraday and day-to-day conditions.

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O8

IDENTIFICATION AND QUANTIFICATION OF VOLATILE NIAS (NON INTENTIONALLY ADDED SUBSTANCES) COMING FROM A STARCH-BASE BIOPOLYMER INTENDED FOR FOOD CONTACT BY APGC-MS/Q-TOF AND GC-MS

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Starch-base biopolymers have been increasingly used for food packaging, because starch is abundant, renewable, biodegradable, low cost, safe and their mechanical properties such as flexibility, high gloss clarity, and tensile strength are suitable for being used as packaging material [1-2]. These biopolymers often contain other polymers such as polylactic acid (PLA) that are also biodegradable under specific conditions. As any food packaging material it must be evaluated to confirm their acceptability. Migration tests are required for this purpose in order to guaranty the consumers' safety. These tests require specific conditions of temperature, time and simulants, which should be selected according to the intended use of the material [3].

In this work, starch-base biopolymer samples as raw starch, pellets and market samples (glasses and dishes) were studied. The extraction process of volatile compounds from the samples was optimized. Extraction solvent selected was methanol and extraction time 60 min. The extraction process of pellets sample was tested for three different pellets shape: pellets without any modification (spheric), pellets smashed under high pressure (lentils) and pellets cryogenically ground in a mill (dust). Finally, lentils were selected since a better extraction of the compounds was achieved. Atmospheric pressure gas chromatography coupled to quadrupole-time of flight mass spectrometry (APGC-MS/Q-TOF) was used for the identification of unknown volatiles coming from starch-base biopolymer. The results were compared with gas chromatography coupled to mass spectrometry (GC-MS). Fifteen compounds were identified, three of them were only detected by APGC-MS/Q-TOF. In addition, migration studies with three simulants, ethanol 10%, acetic acid 3%, and ethanol 95% were performed on market samples. Each test was carried out three consecutive times, as recommended for materials intended for repeated use. Fourteen compounds were detected and ten of them were NIAS. The four compounds with the highest migration values were tetradecanoic acid, hexadecyl ester; hexadecanoic acid, hexadecyl ester, myristyl myristate, 2-acetyl-2,3,5,6-tetrahydro-1,4-thiazine. The intensity of these compounds decreased in the second and third migration tests. The quantification of migrants was carried out by GC-MS.

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O9

ANALYSIS OF ALLERGENS IN FRAGRANCE MATERIALS USING COMPREHENSIVE GAS CHROMATOGRAPHY IN COMBINATION WITH HIGH RESOLUTION TIME-OF-FLIGHT MASS SPECTROMETRY

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Nowadays 1-3% of the Europeans are thought to have allergic reactions to fragrance allergens. In EU, Regulation (EC) 1223/2009 on cosmetic products regulates the obligation about informing the customers of the presence of 26 fragrance allergens, 24 of these are consider chemically fragrances substances in cosmetic products. Labelling guidelines dictates that allergens must appear depending on the concentration and use of that cosmetic products, so accurate analytical methods are a must both for producers and costumers. 2011 new regulation extended the list of allergens up to 90 fragrance ingredients, 54 of which are chemically defined fragrances substances plus isomers.

The 1D GC-MS proposed by IFRA provides a workable solution for many Quality control Laboratories but the possibility of coelutions forces to split the sets of analytes and column, so a lot of time is wasted on multiple separations and calibrations runs, and data reviewing.

In this study, comprehensive two-dimensional gas chromatography (GCXGC) in combination with time-of-flight mass spectrometry was evaluated in order to find a robust one run analytical method.

LECO GCxGC system takes advantage of a dual-stage quad-jet thermal modulator positioned between the two columns and a secondary oven allows independent temperature control of the second dimension column, combined with high acquisition rate, full range TOF mass spectra.

Further experiments with dual MS/FID detection were carried out successfully.

O10

IDENTIFICATION AND QUANTIFICATION OF PCDD/Fs, PCBs AND PBDEs IN ENVIRONMENTAL SAMPLES USING GAS CHROMATOGRAPHY COUPLED TO ORBITRAP MASS SPECTROMETRY

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Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) constitute an important group of ubiquitous organic pollutants of great concern because of their high toxicity and persistence in the environment and their adverse effects on exposed organisms at trace levels. In the last years, besides the PCDD/Fs and PCBs, special interest has been focused on new persistent organic pollutants such as the polybrominated diphenyl ethers (PBDEs). PBDEs have been extensively used as flame retardant additives in a wide variety of products and are easily released into the environment because they are not covalently bound to the material into which they are added. Due to their structural similarity to PCDD/Fs and PCBs, they are suspected to pose toxic effects [1], and they tend to bioaccumulate through the food chain up to humans, resulting in a potential risk for human health.

Due to the stable structure and lipophilic character of these toxicants, they tend to resist degradation, and bioaccumulate in environment, and food chains, and can be transported through air, and water over long distances. They have been identified, in some cases far from their place of use, in a wide range of samples including air, water, sediment, fish, birds, marine mammals, and humans [2].

The potential for human exposure to these compounds makes accurate detection and quantification of these compounds in the environment, particularly in food and animal feed, very important. The aim of this work is demonstrate the feasibility of high resolution accurate mass GC-Orbitrap technology for the targeted analysis of PCDD/Fs, DL-PCBs and PBDEs in food and environmental matrices using a sensitive, fast and robust high throughput method.

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O11

POTENTIAL OF LAB-IN-SYRINGE TECHNIQUE FOR AUTOMATED SAMPLE PRETREATMENT COUPLED ONLINE TO GC-FID

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In this presentation, we give an overview on the development and features of the technique Lab-In-Syringe [1] and its potential for the automation of diverse sample pretreatment approaches. Further, we report on the use of this technique for headspace extraction [2] of environmental contaminants from surface water samples and on-line coupling to gas chromatography (GC) with flame ionization detection using benzene, toluene, ethylbenzene and xylenes as model analytes.

The extraction system was assembled from an automatic syringe pump with a 5 mL glass syringe into which all solutions and air for headspace creation were aspirated. Headspace gas transfer and injection to the GC was accomplished through a secondary syringe outlet through the piston [3] and via a pinch valve-controlled transfer capillary.

Applying the approach of in-syringe stirring [1,3] allowed efficient solution mixing and stirring assisted extraction, which yielded about three-fold increased extraction efficiency. Employment of the syringe as size adaptable extraction chamber allowed both negative pressure application during extraction as well as a very high gas transfer efficiency to the GC. In combination with an unusually high volumetric ratio of headspace to sample and on-column analyte trapping, similarly or higher sensitivity as in former works was achieved [2] yet at room temperature and with simple instrumentation.

Effects of sample salt, detergent, and organic solvent contents were studied and compensated by internal standard method. With exception of co-eluting m-xylene and p-xylene, all analytes were baseline separated with efficiencies of up to 250.000 theoretical plates. Syringe cleaning and extraction over 10 min were carried out in parallel to the chromatographic separation enabling a time of analysis of < 19 min. The method was suitable for surface water analysis including a repeatability of generally < 2 RSD on a 100 µg L^{-1} level, limits of detection of 1-2 µg L^{-1}, and quantitative analyte recovery.

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O12

GAS CHROMATOGRAPHY-ANION ATTACHMENT ATMOSPHERIC PRESSURE PHOTOIONIZATION-HIGH RESOLUTION MASS SPECTROMETRY FOR THE DETERMINATION OF SHORT-CHAIN CHLORINATED PARAFFINS

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Chlorinated paraffins are a highly complex mixtures of polychlorinated n-alkanes with different carbon chain lengths and chlorine content varying from 30 to 70% by mass [1]. They have been widely used as extreme pressure additives in metal working fluids and as flame retardants or plasticizers in rubbers, plastics, paints and coatings [2]. Among them, short-chain chlorinated paraffins (SCCPs) with a carbon chain length from C10 to C13 are of particular concern due to their high toxicity, persistency, and bioaccumulation capability through the food chain. As a consequence, they are listed by the Stockholm Convention as persistent organic pollutant.

SCCPs are currently determined by gas chromatography coupled to mass spectrometry using negative ion chemical ionization technique. However, their chromatographic separation is very difficult because of the high complexity of the SCCP mixtures (more than 10,000 congeners) and errors in the quantification can occur due to mass internal interferences between congeners and homologue groups. Moreover, the response of SCCPs by NICI is highly dependent on the number of chlorine atoms, which makes difficult the selection of the standard mixture for the sample quantification. Recently, chloride anion attachment atmospheric pressure chemical ionization has been proposed as an alternative ionization technique coupled to high resolution mass spectrometry (AA-APCI-HRMS) for the determination of SCCPs, but complex deconvolution procedures of mass spectra are required for the SCCP characterization and quantification [3].

In this work, a gas chromatography-chloride anion attachment atmospheric pressure photoionization-high resolution mass spectrometry (GC-AA-APPI-HRMS) method has been developed for the analysis of SCCPs. AA-APPI ionization has been evaluated employing different dopant/Cl-agent mixtures and temperatures to obtain solely $[M+Cl]^-$ for each congener group, achieving an effective separation of the SCCP congener groups and avoiding internal interferences between them. In addition, the response obtained for SCCP congeners with a different number of chlorine atoms was negligible, allowing the quantification of different congener groups independently of the chlorination degree. The performance of the GC-AA-APPI-HRMS method for the determination of SCCPs was evaluated by analyzing environmental samples of different nature.

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O13

A FASTER WAY TO ELECTROPHORETIC MOBILITY: HOW TO ENHANCE THE ROBUSTNESS OF YOUR CE-MS DATA WITH ROMANCE

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Although LC– and GC–MS are the gold standards in metabolomics, the separation of charged or very polar molecules remains challenging so far. CE provides very efficient separations for such compounds, but the variability of the migration times hampers its application in metabolomics [1]. The use of *effective electrophoretic mobility* (μ_{eff}) has been proposed to circumvent this problem [2], but its application is limited by tedious and time-consuming manual calculations. ROMANCE (RObust Metabolomic Analyses with Normalized CE) is a computationally efficient tool allowing the automated conversion of batches of large CE-MS files from the *time*-scale into the *electrophoretic mobility* scale [3].

ROMANCE is an open-source, multi-core software which can run on any operating system. It takes both profile or centroid mzML files. Herein, we show how the use of *electrophoretic mobility* improves data robustness and comparability in inter- and intra-laboratory environments by analyzing results issued from different CE-MS platforms.

ROMANCE was used to convert files coming from a mix of reference compounds analyzed in the same laboratory but by different operators and on separate days. When the analyses were compared by using the μ_{eff}-scale, the variability of the electrophoretic mobilities of the peaks ranged between 0.9 and 1.2% (%RSD), significantly lower than the 1.3% – 4.5% obtained on the *time*-scale. Then, CE-MS results obtained from different experimental setups (comprising different MS, CE capillary geometries and applied pressures) were studied. The correlation improved in the case of the μ_{eff}-scale with regard to the *time*-scale, allowing the direct comparison of the transformed electropherograms obtained in separate laboratories. We also shown that, by using two reference peaks, ROMANCE can correct the effect of non-constant electric fields being applied during the separation. Finally, deproteinized and fortified human serum samples were analyzed. By using ROMANCE, the detected features were annotated by matching their measured accurate *m/z* and μ_{eff} values to a library of reference standards generated in a separate laboratory. 67 features were annotated with a μ_{eff} error below 3%, showing how ROMANCE allows CE-MS-based data to be shared and exchanged. This approach allows straightforward CE-MS-based identification of metabolites in a comparable way to LC-MS-based workflows.

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O14

ON-LINE SOLID-PHASE EXTRACTION CAPILLARY ELECTROPHORESIS-MASS SPECTROMETRY FOR THE ANALYSIS OF CIRCULATING microRNAs AND THEIR POST-TRANSCRIPTIONAL MODIFICATIONS IN CANCER SERUM

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MicroRNAs (miRNAs) are a class of single-stranded, nonprotein-coding RNAs that are 19–23 nucleotides long [1]. The function of a miRNA is to control gene expression post-transcriptionally, regulating messenger RNA (mRNA). They play a major role in a wide range of normal cellular processes, including cell proliferation, development, and apoptosis. Therefore, deregulation of miRNAs has been associated with different diseases, such as cardiovascular diseases, diabetes, aberrant immune function, and especially cancer [2]. Circulating miRNAs have been found in the extracellular environment, including in various biological fluids, such as the blood, saliva, and urine. The methods currently applied for routine analysis of miRNAs are very sensitive, but do not allow the direct detection of the target miRNAs or their post-transcriptional modifications [3]. These modifications, such as 5'-end phosphorylation and dephosphorylation, or unexpected isoforms with differing ends due to trimming or nucleotide additions, have been reported to affect the stability of miRNA and be a mechanism for the regulation of miRNA activity.

This study describes an on-line solid-phase extraction capillary electrophoresis–mass spectrometry (SPE-CE-MS) method for the purification, preconcentration, separation, and characterization of endogenous miRNAs and their post-transcriptional modifications in serum [4]. First, analysis by CE-MS was optimized using a standard mixture of hsa-miR-21-5p (miR-21-5p) and hsa-let-7g-5p (let-7g-5p). For SPE-CE-MS, a commercial silicon carbide (SiC) resin was used to prepare the microcartridges. Under the optimized conditions with standards, the microcartridge lifetime (>25 analyses) and repeatability (2.8% RSD for the migration times; 4.4 and 6.4% RSD for the miR-21-5p and let-7g-5p peak areas, respectively) were good, the method was linear between 25 and 100 $nmol \cdot L^{-1}$, and the limit of detection (LOD) was around 10 $nmol \cdot L^{-1}$ (50 times lower than by CE-MS). In order to analyze human serum samples, an off-line sample pretreatment based on phenol/chloroform/isoamyl alcohol (PCA) extraction was necessary prior to SPE-CE-MS. The potential of the SPE-CE-MS method to screen for B-cell chronic lymphocytic leukemia (CLL) was demonstrated by an analysis of serum samples from healthy controls and patients. MicroRNAs, specifically miR-21-5p and a 23 nucleotide long 5'-phosphorylated miRNA with 3'-uridylation (iso-miR-16-5p), were only detected in the CLL patients.

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O15

A UNIFI-ED SOLUTION FOR HIGH-RESOLUTION DRUG SCREENING

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As new forms of “designer” drugs threaten public safety, there is an immediate need for advanced ways to identify and classify these complex compounds. Accurate mass instrumentation presents a significant and key advantage over its nominal mass counterpart, i.e., an ability to implement screening methodologies without the requirement of reference material. In this particular workflow the theoretical (expected) exact mass can be determined empirically from the elemental formula. Moreover, fast targeted screening can be performed over hundreds of components contained in a library from a single injection, by means of a truly Independant Data Acquisition (IDA) mode such as MS^e. New "designed" derivatives of psycoactives substances can be efficiently revealed with discovery settings involving common fragment ion, common neutral loss, mass defect filter and/or halogen filter. Several examples of application to toxicolgy screening will be reviewed, showing this technology is a valuable means with which the analyst may ‘prospectively’ target novel psychoactive drugs, or new substances and metabolites where reference material may not yet be available.

O16

SINGLE-PUMP HEART-CUTTING TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY APPLIED TO THE DETERMINATION OF FATTY ALCOHOL ETHOXYLATES

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***In memoriam*

The present communication pretends to be a tribute to Professor Guillermo Ramis Ramos, Full Professor of Analytical Chemistry Department at University of Valencia. He passed away in June of 2017, being a great loss for the Spanish separation science community. Along his distinguished career, Professor Ramis-Ramos worked in different and interesting research lines, being the determination of surfactants in detergents and cleaning products one of the most fruitful and recognized issues. Indeed, this topic arose due to a collaboration with the well-known supermarket company Mercadona S.A., and subsequently continued with Químicas Oro S.A., up to the present day. In particular, the work presented here is focused on the use of two-dimensional chromatography as analytical tool for the characterization and quantification of fatty alcohol ethoxylates (FAEs) present in laundry products. With the selection of an adequate valve opening and closing system, two columns of identical or different nature and using a single HPLC system, the desired objective can be easily achieved. Since the FAEs alcohols do not show chromophore groups, derivatization is required, prior to their chromatographic separation. Thus, in a 1^{st} dimension (column C8 at 25°C), the derivatives were separated according to the length of the alkyl chain by gradient elution, using methanol and water as solvents. The selected segments of the eluate were then transferred to the 2^{nd} dimension (column C8 at 25°C), where the oligomers were separated according to the number of ethylene oxide moles by gradient elution using acetonitrile and water. From a series of standards, the response factors for each homologue were established to correctly characterize the industrial FAEs. The method is particularly useful to characterize FAEs having large average EO numbers, or constituted by mixtures of even and odd series.

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O17

CARBOSILANE DENDRIMERS AND DENDRONS IN PROTEIN SAMPLE PREPARATION

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Protein sample preparation is the bottleneck in protein analysis. Moreover, it usually requires the use of high amounts of reagents and solvents that are not friendly from the environmental point of view. In addition to the extraction and purification, protein sample preparation usually involves the enzymatic hydrolysis of proteins. This step requires the use of non-reusable and expensive enzymes. The emergence of new materials could be the key to innovate in protein sample preparation.

Dendrimers are synthetic macromolecules constituted by layers, called generations, where functional groups or ligands are introduced. The multivalent surface of dendrimers makes them potential host molecules to encapsulate guest molecules. Despite their potential, they have never been proposed in protein sample preparation. A special kind of dendrimers are carbosilane dendrimes. They have a C-Si skeleton which results in a high stability and biocompatibility [1].

Our research group have demonstrated that the interaction between carbosilane dendrimers and proteins can be modulated by controlling the pH, the dendrimer charge, and the dendrimer generation and we have successfuly employed them in the extraction and purification of proteins. Moreover, our research group has also employed different supports (gold nanoparticles, carbon nanotubes, and silica) functionalized with multivalent carbosilane dendrons for the extraction/purification of proteins and for the immobilization of enzymes to hydrolyze proteins. Carbosilane dendrimers and dendrons with different generations and functional groups were employed and results were compared [1-3].

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O18

UHPLC-ESI-MS/MS and UHPLC-ESI-HRMS IN THE CLASSIFICATION AND AUTHENTICATION OF SPANISH PAPRIKA WITH PROTECTED DESIGNATION OF ORIGIN BY CHEMOMETRICS

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Paprika, or chilli pepper, is a red powder seasoning with a characteristic flavor obtained from the drying and grinding of certain varieties of red peppers. The two most common known varieties of paprika in Spain and with protected designation of origin (PDO) come from the regions of La Vera (Extremadura) and Murcia. La Vera paprika is obtained by grinding the totally red pepper fruits of the varieties from the *Ocales* group (*Jaranda, Jariza* and *Jeromín*), and the *Bola* variety. It is characterized by its smoky aroma and taste achieved during the process of drying the peppers using the smoke produced with oak and/or holm oak wood. Depending on the paprika taste, they can be classified into sweet, bittersweet and spicy paprika. In contrast, Murcia paprika is obtained by grinding fully red peppers of the *Bola* variety. Polyphenols can be found among the most interesting bioactive compounds in paprika, and their distribution and content may be attributed to the different red pepper varieties as well as climate conditions. As a consequence, contents of polyphenols and other bioactive compounds can be exploited as a source of analytical data to establish product classifications, and the evaluation of food quality and the detection of adulterations can thus be based on polyphenolic and metabolomic approaches [1].

In the present work, a UHPLC-ESI-MS/MS (triple quadrupole) method was developed to determine 37 polyphenols in paprika samples. UHPLC-ESI-HRMS in a Q-Exactive Orbitrap was also employed to obtain paprika polyphenolic fingerprints by means of a customized target accurate mass database of 54 polyphenols using TraceFinder™ software. Furthermore, UHPLC-HRMS paprika metabolomic profiles were obtained at a resolution of 70,000 FWHM (full width at half-maximum). 111 samples belonging to La Vera and Murcia Spanish PDOs (including sweet, bittersweet and spicy varieties), as well as 15 samples obtained from the Czech Republic were analyzed. Polyphenolic and metabolomic profiling data were employed as a source of potential descriptors to be exploited for the classification of paprika according to PDO and region of production by principal component analysis (PCA) and partial least squared-discriminant analysis (PLS-DA). The plot of scores showed successful separations in accordance to both PDO and production region. Moreover, a discrimination between Murcia and Czech Republic paprika varieties (sweet and spicy) was also possible. The most remarkable polyphenols on each type of paprika PDO and variety were also identified.

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O19

DETERMINATION OF THE CONTENT OF CALYSTEGINES IN TOMATO-BASED PRODUCTOS APPLYING LC-HRMS

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Tomato (*Solanum lycopersicum*) is the most produced vegetable worldwide, reaching 170.000 million kg, according to the FAO 2014 data [1]. This vegetable belongs to Solanaceae family, which is well-known for containing tropane alkaloids [2]. After the discovery of calystegines in 1988 and their structure elucidation, a study of the occurrence of calystegine in Solanaceae family was developed because of their closely related structure to tropane alkaloids [3]. Calystegines are water soluble non-esterified alkaloids characterized by having 3, 4 or 5 hydroxyl groups and named calystegines A, B or C, respectively. They inhibit glycosidase and some of them are potent inhibitors of β-glucosidase and α-galactosidase [2].

Taking into account the high consumption of tomato and tomato-based products (crushed, fried and marmalade tomato), a study of the occurrence and concentration variation of 7 calystegines (A3, A5, B1, B2, B3, B4 and C1) has been performed. For that purpose, a solid-phase extraction with methanol/water (50/50, *v*/*v*) was developed, and a liquid chromatography equipped with an ACE HILIC-A column and coupled to high resolution mass spectrometry has been carried out (LC-HRMS-Orbitrap). The validation of the method was performed evaluating calystegines B1, B3, B4 and C1, which were not naturally present in the sample used for validation. Recoveries ranged from 70 to 120 % with RSD lower than 20 % were obtained and limits of quantification (LOQ) were set at 0.1, 0.25 and 0.5 mg/kg.

Finally, 12 different samples were analyzed, comprising 4 crushed tomatoes, 4 fried tomatoes and 4 tomato marmalades. Calystegine A3 and B2 were detected in all the analyzed samples at concentrations ranging from 1.5 to 19.0 mg/kg and from 0.4 to 10.5 mg/kg, respectively. Calystegine B3 was detected in all the fried tomatoes as well as in two crushed tomatoes and one marmalade (0.4 to 2.9 mg/kg). Calystegine A5 was detected in all the samples, but only at concentrations higher than LOQ in 3 samples (0.5 to 0.7 mg/kg). Additionally, one marmalade sample contained 1.9 mg/kg of calystegine B1.

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O20

DIFFERENTIATION OF OLIVE OILS FROM THE SAME BOTANICAL VARIETY (ARBEQUINA) ACCORDING TO THEIR GEOGRAPHIC ORIGIN USING CHROMATOGRAPHIC TECHNIQUES AND CHEMOMETRIC TOOLS

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Olive oil is a highly consumed product, either alone or as an ingredient in different foods. Europe is the world region with the highest production of olive oil, and within this, Spain. Olive oil characteristics depends of parameters related especially with the botanical variety, but also of others associated with geographic area. In consequence, the oils obtained in different regions could differ in quality and composition [1]. Triglycerides content in vegetable oils is an information useful to confirm their authenticity, detect possible adulterations and know the composition in mixtures, because these constitute a characteristic fraction of the oils.

The aim of this study is the development of a method for the efficient differentiation of olive oils from the same botanical variety (‘Arbequina’) depending on their geographic origin using chemometric tools. Virgin olive oil from ‘Arbequina’ is highly acclaimed on the international market due to its sensorial quality. It is important to detect possible adulterations in olive oil, which is more expensive than other types of vegetable oils [2].

Triacylglycerides chromatographic fingerprint of 69 samples of olive oils from Catalonia and the South of Spain, have been obtained by high-performance liquid chromatography coupled to a charged aerosol detector and by high-temperature gas chromatography with a flame ionization detector (FID). SIMCA and PLS-DA classification models were developed after a suitable preprocessing and a PCA exploratory analysis. The main performance parameters (sensitivity, specificity and inconclusive ratio) [3] indicate that a good differentiation was obtained between samples from different geographic origins since values higher than 77% were obtained for the first two parameters and lower than 25% for the inconclusive ratio.

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O21

DETECTION AND QUANTIFICATION OF CASEIN AND OVALBUMIN IN CHILEAN WINES WITH UHPLC/ESI-QQQ-MS/MS AND UHPLC-ESI/QTOF-MS/MS

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Casein and ovalbumin are used in the wine clarification process to promote interactions with undesirable compounds, such as polyphenols and tannins. This kind of proteins may trigger allergic reactions in susceptible individuals, therefore their presence in wines could became a human health risk, especially when is not reported. For this reason, the European Union established that those concentrations higher than 0.25 mg L^{-1} should be declared [1]. The objective of this work was to establish two methods by LC-ESI-QQQ-MS/MS and LC-ESI-QTOF-MS/MS to identify and quantify these proteins in Chilean wines.

Proteins were extracted combining the use of ultrafiltration membranes and precipitated with organic solvents. Thereafter, proteins were digested with trypsin with the use of ultrasound energy. A face-centered central composite design with two central points was selected to optimize the enzymatic digestion, establishing a digestion time of 3 minutes and an enzyme/protein ratio of 1:10. Peptides separation was carried out on Phenomenex Kinetex XB Core-Shell C_{18} column (100 mm x 4.6 mm, 2.6 µm), at 35°C, using a mobile phase composed of ultrapure water and acetonitrile, both with 0.1 % (v/v) formic acid. The results were analyzed by a QQQ and QTOF mass analyzer. Marker peptides for quantification were defined among the most abundant and stable. For a selective evaluation, quantification was performed in MRM mode, using an isotopically labeled peptide as internal standard.

With the QQQ, two pairs of precursor peptide - product peptide for α and β-casein and ovalbumin can be identified, using an injection volume of 50 µL. However, using LC-QTOF-MS we were able to identify 7, 4 and 5 pairs of precursor-product peptides for α, β-casein (two of these have not been reported in the literature) and ovalbumin respectively, with an injection volume of 2 µL. This method also allowed to identify the characteristic peptides of k-casein, which was not possible using the QQQ. Regarding the quantitative analysis, the LOD and LOQ ranged from 4.7 to 8.5 µg L^{-1} and 10 to 20 µg L^{-1}, respectively, working in MRM mode with the QQQ, while with the QTOF were higher, between 10-60 µg L^{-1} and 50-200 µg L^{-1} for LOD and LOQ, respectively. The results show the advantage of using a QTOF mass analyzer to detect and identify as many peptides as possible, while using QQQ for its exact quantification. Sixty samples of Chilean wines were analyzed, finding 14 samples with high levels of casein and ovalbumin later recommended by the International Organization of Vine and Wine.

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Y1

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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Y2

NEW ANALYTICAL PROPOSAL TO MONITOR VOLATILE ORGANIC METABOLITES AS BIOMARKERS OF BACTERIAL SPOILAGE IN COSMETICS

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Cosmetics do not need to be sterile, but they must be adequately preserved from microbial contamination. However, for several reasons (water content, storage conditions…), microbial growth may occur, representing an important risk for consumers health [1]. To provide consumers with microbiologically safe cosmetics products is critical and, although classical microbiological tests are available, they are long-time consumption and require several experimental steps. Therefore, the development of simple and fast analytical methodology to detect microbial contamination is required.

Microorganisms generate volatile organic compounds (MVOCs) during metabolic processes, and some of these metabolites could be specific of microbiota groups (Gram +/-), genera and/or species. On this basis, the hypothesis to design this work was to look for a potential relationship between MVOCs and specific bacteria. In addition, previous studies by our research group have proven that the use of solid-phase microextraction (SPME) is a valuable, fast and *in-situ* tool for the MVOCs monitoring, and the use of gas chromatography coupled to mass spectrometry (GC-MS) allows an unequivocal identification of the extracted VOCs. The selected compound can be used, in this way, as biomarkers of the microorganisms present in the cosmetic formulations [2]. Another key idea in this approach is that bacteria produce different metabolites depending on the available nutrient resources. In this framework, two *Gram negative* bacteria were first selected to check the suitability of the research scheme, named *Escherichia coli* and *Proteus mirabilis,* due to both their frequent occurrence in cosmetic spoilage and their pathogenicity. Bacteria were exposed to a certain culture medium containing known food sources, and the generated metabolites by the different bacteria were monitored and identified by SPME-GC-MS. Several MVOCs were identified as specific biomarkers for each one of the studied microorganisms, whereas other of the identified volatile compounds can be used as general indicators of microbial presence.

This talk will show the design and development of this original approach and the results of its practical application to the control of microbial contamination in real cosmetic samples.

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Y3

COMBINED USE OF γ-CYCLODEXTRIN AND CHIRAL IONIC LIQUIDS FOR THE ENANTIOMERIC SEPARATION OF HOMOCYSTEINE BY CAPILLARY ELECTROPHORESIS

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Ionic liquids (ILs) have attracted great attention in the last years in analytical chemistry being widely used in extraction and separation techniques [1]. ILs are a group of salts with melting points below 100 °C formed by bulky organic cations and organic or inorganic anions which confer them unique properties as high conductivity, good thermal stability, high miscibility in water and organic solvents, etc. [2]. ILs which has a chiral cation and/or anion are called chiral ionic liquids (CILs). The use of CILs as new potential selectors for enantiomeric separations by capillary electrophoresis (CE) is a hot topic in the field of chiral separations. Even though they can be used as sole chiral selectors, most of the works reported in the literature were focused on the study of their synergistic effect when they are used in combination with other selectors like cyclodextrins (CDs), antibiotics or polysaccharides [3].

The aim of this work was to develop new analytical methodologies by CE to achieve the enantiomeric separation of homocysteine with different CDs and CILs as sole chiral selectors, and to evaluate the discrimination power of the combined use of both kinds of chiral selectors. Homocysteine is a sulfur containing non-protein amino acid related with the metabolism of methionine which is also considered a biomarker in cardiovascular and degenerative diseases [4]. To carry out this study, homocysteine was derivatized with FMOC (9-fluorenylmethoxycarbonyl chloride) and eleven neutral CDs and five CILs were evaluated. The use of a phosphate buffer at pH 7.0 with a dual system formed by γ-CD and (R)-N,N,N-trimethyl-2-aminobutanol-bis(trifluoromethane-sulfon)imidate (EtCholNTf$_2$) enabled to achieve the enantiomeric separation of homocysteine in a short analysis time (~11 min) with a high resolution (8.0). Interestingly, the combination of both selectors originated the reversal of the migration order for homocysteine enantiomers with respect to that observed when both selectors were used in a single system. This fact could indicate that the mechanism for the chiral recognition in the dual system would be different from that existing in a single one.

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Y4

FLOW APPROACHES: AUTOMATION OF SAMPLING AND SAMPLE PREPARATION AS A FRONT END TO HPLC

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Chromatography and, in general separation techniques, are enabling analytical techniques that offer unmatched performance for real sample analysis. They are still deemed nowadays the workhorse for understanding the world of complex mixtures we live in. Whereas most of the efforts are currently directed on hyphenating different separation techniques and including more and more dimensions for enhancing the selectivity and sensitivity of the assays, sampling and sample preparation are the real throughput bottleneck in the analytical laboratory.

In this contribution we would like to present a compilation of the work done in the field of flow approaches, that is, the (usually low) pressure driven fluid manipulation in closed manifolds, e.g. FIA and SIA, in order to automate the sampling and sample preparation as a front end to liquid chromatographic assays. Those hyphenated techniques also allow the design of experiments that otherwise would be difficult to implement as e.g. kinetic monitoring.

Several publications from the last two years will be presented, aimed at legacy and emergent organic pollutants in pharmaceutical, clinical and environmental analysis, and exploit liquid and solid sample introduction through microfiltration [1] and tangential filtration [2], liquid-liquid microextraction (LLME) [3] and micro-solid phase extraction (SPE) [4] for flow-through preconcentration and matrix cleanup and strategies prior to online hyphenation to reversed phase HPLC. As an added feature, the inclusion in those manifolds of 3D printed fluidic platforms and nanomaterials as sorbent phased will be discussed in detail.

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Y5

BIOACCUMULATION OF PERFLUOROALKYL COMPOUNDS IN MARINE ECHINODERMS: RESULTS OF LABORATORY-SCALE EXPERIMENTS WITH *HOLOTHURIA TUBULOSA*

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In the present work, the bioaccumulation of six PFCs (perfluorooctane sulfonic acid, PFOS, and five perfluoroalkylcarboxylic acids, C4-C8) was assessed by using the echinoderm *Holothhuria Tubulosa* bioindicator. Semi-static batch experiments, at three different spiked concentrations (0.1, 0.5 and 1 mg L^{-1}), were conducted to establish the relationship between concentrations in water, sediment and biota over 197 days. The sample treatment for the determination of compounds in sediments and biota involves steps of lyophilization, solvent extraction and clean-up of the extracts with dispersive sorbents. PFCs were then analysed by liquid chromatography–tandem mass spectrometry.

During contaminant exposure, detectable levels of the six compounds were found in all samples collected. Mean concentrations were higher in sediments than in water samples. This fact is explained by the strong adsorption of these compounds into sediments [1]. Sediment-water distribution coefficients (log K_d) were in the range 0.11 (C4) to 2.46 (C8).

Beside this, clear PFCs accumulation was observed in Holothuria organisms. The uptake of PFCs was very rapid, reaching the maximum between 22-38 days of assay. Bioaccumulation factors (mean log BAF: 1.16 - 4.39) and biota sediment accumulation factors (mean log BSAF: 1.37 - 2.89) indicated a high bioaccumulation potential for the target compounds. Both parameters increased with perfluorinated carbon chain length ($R^2 > 0.93$; $p < 0.05$). In organ-specific distributions of PFCs, greater concentrations were found in intestine than in gonads. Also, male specimens showed higher concentration levels than female (student t test: $t_{cal} = 2.788$, $t_{tab} = 2.262$; $p < 0.05$). These data form a detailed accounting of PFC fate and distribution in the marine environment highlighting accumulation at lower trophic levels, a potential source for contamination in higher organisms [2-3].

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Y6

ANALYTICAL METHOD DEVELOPMENT FOR THE DETERMINATION OF HYDROPHILIC MARINE BIOTOXINS IN SEAWATER

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During last decades, the presence of marine biotoxins (MBTs) in coastal areas has increased supposing a threat to the human health due to their toxic properties and capability to bioaccumulate along the food chain. Many regulations have been established for the control of MBTs in seafood and new analytical methodologies have been developed to being used as monitoring tools. However, the direct determination in seawater is not easy, especially for the most hydrophilic MBTs.

In this work, it has been developed an analytical method based in hydrophilic interaction liquid chromatography (HILIC) coupled to high resolution mass spectrometry (HRMS) to determine the presence of hydrophilic MBTs directly in seawater. These hydrophilic MBTs are: tetrodotoxin (TTX); domoic acid (DA); gonyautoxin-5 (GTX-5); decarbamoylsaxitoxin (dcSTX) and neosaxitoxin (Neo).

Due to the different chemical properties of these compounds, different methods of extraction were employed in order to achieve the highest recoveries and to eliminate the high content of salts in seawater. Different conditions of pHs and sample volumes were considered for: solid phase extraction testing different stationary phases, liquid-liquid extraction with different solvents, solid liquid extraction using activated charcoal and assisted by ultrasounds and dialysis with a 100-500 Da cellulose membrane.

The chromatographic separation was carried out in an Acquity ultra-high-performance LC system (Waters, Massachusetts, USA), using as stationary phase a HILIC column (LUNA® 150 × 2.0 mm, particle size 3 µm from Phenomenex) and for the mobile phase the composition was 90% acetonitrile and 10% of 5 mM ammonium formate buffer at the flow rate of 0.3 ml/min. The LC system was coupled with a heated electrospray ionization (HESI) source, working in positive mode, to a Q-Exactive (Thermo Fisher Scientific, San Jose, CA, USA) mass spectrometer with a hybrid quadrupole–Orbitrap analyser. Data dependent scan was used for the acquisition; full scan (m/z 300–1500) with a resolution of 70000 full widths at maximum height (fwhm) in parallel to tandem mass spectrometry of the selected toxins. Quantification was performed using matrix-matched calibration curve of all compounds. Standards of each compound were purchased from Cifga with a purity ranging from the ≥96% to the ≥99%.

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Y7

A FULLY AUTOMATED APPROACH FOR THE ANALYSIS OF 37 PSYCHOACTIVE SUBSTANCES IN WASTEWATER BASED ON ON-LINE SPE-LC-MS/MS

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The consumption of psychoactive substances, legal or illegal, is widespread in our society. According to the last World Drug Report of the United Nations Office on Drugs and Crime, 255 million people between 15 and 64 years used illicit drugs at least once in 2015 [1]. Psychoactive substances are also medically prescribed to treat specific human health disorders. Their consumption, prescribed or not, has significantly increased in the last years. [2].

The objective of this work was to develop and validate a multi-residue analytical method based on on-line solid phase extraction and liquid chromatography tandem mass spectrometry (on-line SPE-LC-MS/MS) detection for the simultaneous determination of 37 psychoactive substances in raw wastewater. The list of target psychoactive substances included illicit drugs such as cocaine compounds, amphetamine type stimulants, hallucinogens, opiates and cannabinoids; new psychoactive substances, and psychoactive pharmaceuticals such as benzodiazepine-type anxiolytics, antidepressants, sedatives, antipsychotics, and hypnotics.

The methodology developed was validated in terms of linearity, recovery, repeatability, sensitivity and matrix effects in wastewater. Linearity expanded over four orders of magnitude for most compounds (0.1-2000 ng/L). Absolute recoveries were low (below 60%), however, the use of isotopically labeled compounds corrected for analyte losses during the extraction process as well as matrix effects (relative recoveries between 80 and 120 % were obtained for all analytes). Repeatability of the method was satisfactory for most analytes (RSD < 13%). Limits of detection and quantification in wastewater were below 7 and 23 ng/L, respectively, for most of the analytes. The worst sensitivity values were observed for amphetamine, cannabis metabolites, lormetazepam and caffeine (with LOQs between 60 and 257 ng/L).

Application of this method to real raw wastewater revealed the presence of most of the investigated compounds in the water samples analyzed, in some cases at relevant levels. The most abundant compounds were the stimulant caffeine (average concentration of 53.8 µg/L), followed by stimulant pharmaceutical ephedrine (2.3 µg/L), the cocaine metabolite benzoylecgonine (2.2 µg/L), cocaine (1.3 µg/L), the THC metabolite 11-nor-9-carboxy-THC (1.1 µg/L), and the antidepressants venlafaxine (0.8 µg/L), citalopram (0.4 µg/L) and sertraline (0.4 µg/L).

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Y8

LAYER-BY-LAYER DEPOSITION *VERSUS* ELECTRODEPOSITION TO PREPARE SILVER-BASED COATINGS ONTO BRAID SOLID-PHASE MICROEXTRACTION FIBERS FOR THE DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN WATERS

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Solid-phase microextraction (SPME), developed by Pawliszyn in 1990, is a widely employed technique for ultra-trace determination of pollutants in waters. SPME advantages over conventional sample preparation techniques include low sample volume requirements, minimization or elimination of the usage of organic solvents in the sample preparation step, fastness, high sensitivity, and combination of extraction and preconcentration in one single step.

SPME fibers require a solid support resembling a fiber, mainly of metallic nature, with one centimeter of coating on one extreme. Commercial available coatings (roughly 6) are made of polymers or a mixture of them. Although these coatings have demonstrated an excellent extraction capability, their selectivity is low. In addition, their chemical, mechanical and thermal stability narrow down their use in very complex samples or under more aggressive extraction conditions. Thus, trends on the field focus on the development of novel geometrical supports disposition for the fibers together with the search of novel coatings including avant-garde materials such as metallic nanoparticles [1-3].

In this study, we report novel geometrical braid-SPME support fibers coated with (a) silver nanoparticles (AgNPs) or (b) silver dendrites. Silver dendrites-based SPME coatings were prepared through an electrochemical deposition, and the AgNPs-based SPME coatings were prepared through a layer-by-layer approach. The developed fibers were applied to the determination of polycyclic aromatic hydrocarbons in environmental waters.

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Y9

CE-MS FOR METABOLOME FINGERPRINTING OF *LEISHMANIA AMAZONENSIS* INFECTED MURINE MACROPHAGES: DECIPHERING L-ARGININE METABOLISM

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About 350 million people are considered at risk of contracting leishmaniasis, and its annual incidence is estimated in 1.5 million cases for cutaneous manifestations and 300.000 cases for visceral manifestations. *Leishmania amazonensis* induces cutaneous and/or diffuse cutaneous manifestations [1].

L-arginine is an essential amino acid for the survival of *Leishmania* and to define the fate of the infection, influencing the host-parasite interaction. Due to the relationship with the polyamine pathway, and therefore ionizable compounds, CE-MS was the technique of choice for a non-targeted metabolomics study aiming to obtain a broad picture of metabolic changes in BALB/c-murine macrophages infected with *L. amazonensis* wild type (La-WT) or arginase knockout (La-arg$^-$) and compared to uninfected macrophages.

Samples were extracted and analyzed as optimized in our previous work [2]. The instrument consisted of a capillary electrophoresis system (7100 Agilent) coupled to a TOF Mass Spectrometer (6224 Agilent) equipped with an ESI source, whereby the CE mode was controlled by MassHunter Workstation software (B.06.00, Agilent). Identification was performed across the entire profile of 135 features by searching *m/z* against CEU Mass Mediator [3]. Putative identities were assigned to *m/z* values for metabolite features considering i) mass accuracy (maximum mass error 10 ppm); ii) isotopic pattern distribution; iii) possibility of ion formation and iv) adduct formation. For as many metabolites as possible, authentic standards were analysed, both separately and spiked into quality control samples to validate their identification. All features identified as fragments, dimers or ringing artefacts, as described by Godzien et al. 2015 [4], were removed from the dataset. Using this platform, more than 89 compounds were identified as statistically significant in La-WT-infected macrophages compared to uninfected ones. In addition, 80 metabolites were significantly altered in La-arg$^-$-infected macrophages compared to uninfected. In the comparison of La-WT-infected versus La-arg$^-$-infected, only 14 metabolites were significantly altered.

L. amazonensis infection increased the levels of proline, glutamic acid, glutamine, L-arginine, ornithine and putrescine, activating the polyamine pathways. However, an increase of citrulline levels indicates the metabolization of L-arginine by iNOS and/or arginine deiminase. The absence of parasite arginase activity reduces the amount of ornithine, proline and tripanothione in infected macrophages, but increases argininic acid and citrulline. Altogether, the parasite arginase impacts the metabolomic fingerprint of *L. amazonensis*-infected macrophages.

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Y10

STUDY OF DIABETIC NEPHROPATHY IN HK-2 CELLS USING A METABOLOMIC PLATFORM BASED ON LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY

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One of the most frequent complication of diabetes is diabetic nephropathy (DN), which is the leading cause of end-stage kidney disease worldwide. DN implies the chronic loss of the kidney function and also causes a serious impact on the human health, such as a high heart attack risk. These factors make DN a severe disease. Since the number of end-stage kidney disease patients increases every year, DN has become a public health issue.

The metabolomics approach to DN is particularly relevant for the identification of potential biomarkers which help unveiling the molecular mechanisms of DN [1]. In this context *in vitro* models present important advantages; for example, the experimental conditions are more controlled and, compared to *in vivo studies,* they have less ethical issues.

The purpose of this work was to study for the first time an *in vitro* model of high glucose (HG)-induced metabolic alterations in HK-2 cells using a non-targeted metabolomics approach. To this end, a liquid chromatography-mass spectrometry platform was developed to find the metabolites which were affected by HG. Both intracellular and extracellular medium from HK-2 cells exposed to HG, low glucose (glucose control) or mannitol (osmotic control) were analyzed using two complementary chromatographic modes, reversed-phase liquid chromatography (RPLC) and hydrophilic interaction (HILIC) for expanding the metabolite coverage. Non-supervised principal components analysis and supervised partial least square discriminant analysis showed differences among the three groups of samples and the molecular features with a high variable in the projection were selected as relevant molecules. Some metabolites were found in both fluids but others were found just in one fluid. These metabolites were mainly amino acids and carbohydrates.

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Y11

IMPROVING TRANSFERRIN PURIFICATION FOR THE DETECTION OF ABERRANT GLYCOSYLATION IN INFLAMMATROY DISEASES

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Inflammatory diseases have been described to alter the glycosylation pattern of proteins, in particular, changes in sialylation, fucosylation and glycan branching [1]. Transferrin is an acute-phase glycoprotein that is responsible of the iron transport through the blood plasma, but its glycosylation was described to be altered in some inflammatory diseases such as rheumatoid arthritis (RA) [2]. Collagen induced arthritis (CIA) in mice resembles human RA in terms of disease course and also in the response to commonly used pharmaceuticals [3]. Thus, CIA could be considered a perfect model to study the efficacy of novel drugs and to evaluate the glycosylation changes derived from arthritis. Additionally, working with mice models of human pathologies is more cost-effective and easy.

In this work, an immunoaffinity chromatography (IAC) purification was developed to properly isolate Tf from serum samples. This methodology was optimized to purify human as well as mouse transferrin (hTf and mTf) from serum samples testing different conditions to remove nonspecific proteins and thereby increasing the purity of Tf. Depletion kits prior to IAC purification were also evaluated. SDS PAGE electrophoresis as well as nanoLC-MS^n analysis of the eluted IAC fractions were used to monitor the performance of Tf purification. hTf and mTf from control serum samples were purified by IAC and their glycan isomers were analyzed by zwitterionic hydrophilic interaction capillary liquid chromatography coupled to mass spectrometry (μZIC-HILIC-MS) [4]. A healthy glycosylation pattern of these glycoproteins was established to properly identify alterations in Tf glycans caused by certain pathology. Finally, to detect modifications in mTf glycosylation in mice suffering from CIA, relative quantification of mTf glycans was carried out using a glycan reductive isotope labelling strategy with [$^{12}C_6$]/ [$^{13}C_6$] aniline (pathological versus control serum samples) [5]. These mTf alterations in CIA could be useful, in the future, to find novel glycan biomarkers for the diagnosis of RA in humans.

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Y12
UHPLC-IMS-QTOF MS METABOLOMICS FOR BIOMARKER DISCOVERY OF ORANGE DIETARY INTAKE

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Nowadays, metabolomics and the other "-omics" techniques are growing due to their great potential and versatility in many research fields such as health research and nutrition, with a high interest in the human welfare. Regarding the nutrition field, metabolomics can provide a complete picture of the dietary intake by measuring the profile of metabolites in biological samples. Therefore, it can be applied to discover new biomarkers of nutritional exposure and help to unravel the molecular mechanisms whereby diets affects positively or negatively to health [1]. The arrival of new and powerful analytical technologies like ion mobility separation coupled to high resolution mass spectrometry (IMS-HRMS) has provided new tools to facilitate the complicated task of biomarkers elucidation in metabolomics. IMS allows to maximize the detection of markers without increasing the analysis time, obtaining additional structural information (independent of the retention time) given by the collision cross-section (CCS) of the molecules. In addition, the fast time scale of the IMS separations (a few ms) facilitates its coupling after ultra-high pressure liquid chromatographic (UHPLC) separations, with 3-6s peak widths [2].

The aim of this work is to investigate the biomarkers associated with orange consumption in plasma samples taken in acute (4h after consumption) and in a medium-term intervention study (after 1 month of continued intake). This type of study is intended to provide more reliable results on the real diet and avoid the usual bias response of the commonly applied epidemiological studies questionnaires [1]. The crossover, randomized trial enrolled 30 healthy participants (aged 25±2.8 y) and oranges or control water (with sucrose) were provided. Plasma samples were collected at baseline (after fasting), and at 4h postprandial. Samples were treated with acetonitrile for deproteinization followed by centrifugation. Then, 1µL of the supernatant was directly injected in both RP and HILIC chromatography. The UHPLC-IM-QTOF MS data were extracted and processed with *Progenesis QI* and finally statistically analysed by multivariate analysis in order to highlight the potential biomarkers of orange consumption. As preliminary results, stachydrine and betonicine have been tentatively identified as markers of orange consumption in the acute intervention study.

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Y13

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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Y14

ISOLATION AND CHARACTERIZATION OF A- AND B- TYPE OF COCOA PROANTHOCYANIDINS BY HPLC-QTOF-MS/MS

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Cocoa powder has been described as the 4th richest dietary source of polyphenols [1], with increasing applications in food, pharmaceutical and cosmetic industries [2] . In general, cocoa flavonoids consists of B-type procyanidins with a degree of polymerization (DP) up to 12 units. However, better elucidation is still a challenge due to the lack of separation of enantiomers and low sensitivity of traditional low-resolution MS. However, the application of the latest technological improvements in mass spectrometry may allow a deeper characterization of main cocoa flavonoids.

Thereby, the aims of this work were:

- Fractionation of cocoa procyanidins by preparative HPLC using a diol column.
- Characterization and linkage elucidation of procyanidins by QTOF-MS/MS analysis.

As expected, theobromine, caffeine, and theophylline -in less amount- were the main alkaloids detected in positive ionization mode. (-)-Epicatechin was the major flavan-3-ol followed by (+)-catechin. Regarding procyanidins, polymers up to decamers were identified. Overall, procyanidins mainly consisted of B-type species. Polymeric procyanidins between degree of polymerization (DP) 2 - 6 were detected as singly-charged ions, but those containing DP ≥ 7 were found as multiply-charged ions in the negative ESI mode. About 127 procyanidins were elucidated, including dimer, trimer, tetramer, pentamer, and hexamer procyanidins with *m/z* equal to 577.1358, 865.1993, 1153.2624, 1442.3301, 1730.3923, respectively. Fragment ions produced in MS/MS experiments followed well-known theoretical fragmentation pathway mechanisms such as quinone methide (QM), retro-Diels-Alder (RDA) as well as heterocyclic ring fissions (HRF). In general, B-type interflavan linkage were more frequent than A-type species, being identified by possessing 2 Da less than those of the B-type species. For example, trimer and tetramer species were detected at *m/z* 865.1918 and 863.1868 and 1153.2624 and 1149.3679 (-4 Da) for B- and A-types, respectively. Interestingly, the presence of one and two A-type linkages and glucose moiety (e.g., β-galactopyranose, α-arabinopyranose and glucopyranosyl) attached to procyanidins was also found. Therefore, dimer, trimer, tetramer with *m/z* 739.1888, 1025.2326, 1313.2987, respectively are reported.

In addition, the presence of (epi)afzelechin-(epi)catechin (m/z 561.1358), (epi)afzelechin–(epi)catechin–(epi)catechin (m/z 849.2046) as well as (epi)afzelechin-(epi)afzelechin–(epi)catechin (m/z 833.1250), and novel dimer, trimer, pentamer, hexamer with m/z 575.1195, 849.2045,

1425.3268, 864.1901 ($[M-2H]^{-2}$) in cocoa is reported for the first time. These observations highlight the importance of high resolution MS as useful tool for the characterization of cocoa proanthocyanidins as well as for further studies involving their detection in the organism upon metabolization.

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Y15

DETERMINATION OF PIGMENTS IN EDIBLE OILS BY LC-MS: CHARACTERIZATION AND FRAUD DETECTION

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Olive oil is one of the most widely consumed product in many parts of the world and it has always been target of adulterations with either vegetable oils or with the addition of pigment dyes. The color is an important characteristic for consumers to evaluate its quality, being the green color considered as high quality. Different pigments such as carotenes, carotenoids and chlorophylls are responsible of olive oils color but due to the production processes or inadequate storage conditions, color can change from green to yellow-brown. Thus, in order to regreen the poor quality oils, instead of adding 20-30% of extra virgin olive oil as it is established, a fraudulent practice consisting in the addition of different pigments has been detected. However, the variation of the concentration of natural pigments with climate conditions, harvesting time and olive cultivars must be taken into account when detecting potential fraudulent samples [1,2].

In this work we describe the UHPLC-MS/MS method developed for the analysis of pigments in edible oils. The chromatographic separation of all pigments is performed using an Accucore C18 reversed-phase (100 x 2.1 mm, 2.6µm particle size) column under a quaternary gradient elution (water:methanol:acetone:acetonitrile) providing the separation of the analytes in less than 15 minutes. In order to couple the chromatographic method to mass spectrometry, different atmospheric pressure ionization sources (ESI, APCI and APPI) have been evaluated. The best sensitivity was provided by APPI although APCI could also be considered for routine analysis since the sensitivity required for the quantification of these analytes in olive oils is good enough. Moreover, tandem mass spectrometry studies have also been performed to characterize the target compounds and to select the most characteristic and abundant product ions to propose a quantitative UHPLC-MS/MS method in MRM mode. Additionally, high resolution mass spectrometry has also been evaluated for this application to overcome some interference problems and to allow retrospective analysis for non-target pigments.

For the analysis of edible oil samples an extraction and clean-up procedure based on silica SPE and saponification have been applied before the UHPLC-MS analysis. Finally, for the characterization and fraud detection, 65 edible oil samples from different parts of Spain (Anadalusia, Catalonya, Basque Country, etc.) have been analyzed.

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Y16

ANALYSIS OF 52 PESTICIDES IN FRESH FISH MUSCLE BY DISPERSIVE SOLID PHASE EXTRACTION WITH QUECHERS FOLLOWED BY UPLC-MS/MS ANALYSIS.

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Pesticides are among the most used chemical substances worldwide. However, their investigation in the environment has very much focused in the water compartment and in the occurrence of the so called PBTs (persistent, bioaccumulative and toxic compounds), whereas the occurrence of more polar compounds in other compartments and in particular in biota has been little studied. This may be in part due to the difficulty of their analysis in this complex matrix and to the consequent scarcity of methods available for this purpose. In this context, the main objective of the present work was to develop a multi-residue analytical method based on LC-MS/MS analysis for the determination of a range of different polarity pesticides in biota (fresh fish muscle) and to apply it to a set of real samples in order to, first, prove its merit and performance and, secondly, have a first picture of the occurrence of the compounds investigated in the matrix under study. The method should in addition provide the necessary sensitivity to measure them at levels below the general default maximum residue level (MRL) of 10 ng/g and be as time- and cost-effective as possible to allow routine application. Under these premises, a method based on a QuEChERS extraction approach and UPLC-MS/MS analysis for determination of fifty-two pesticides in fresh fish muscle was developed. Quantification was carried out using an isotope dilution approach. The method developed was satisfactory in terms of trueness (relative recovery between 80-116% and relative standard deviation below 20%) and sensitivity (method reporting limits were between 0.01 and 0.9 ng/g f.w.). Its application to fish samples collected in the Adige River basin revealed the presence of five of the target pesticides (e.g., irgarol, metolachlor, quinoxyfen, terbutryn, acetamiprid) at quantifiable levels.

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P-CPA-01

CREATION OF A DATABASE OF HUMAN AND VETERINARY DRUGS CONTAINING THEIR COLLISION CROSS SECTION AS NOVEL CHARACTERIZATION PARAMETER

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The integration of ion mobility spectrometry (IMS) in traditional liquid chromatography-mass spectrometry (LC-MS) workflows provides complementary information to retention time and mass spectra, the so-called collision cross section (CCS). Therefore, this molecular descriptor may potentially be used for the identification of human and veterinary drugs [1]. This approach is especially interesting in the field of metabolomics where a wide number of compounds from different chemical families are detected and compound identification remains as the main challenge. Therefore, the creation of CCS databases can be helpful for molecular identification. So far, only a reduced number of these drugs have been characterized in terms of CCS, limiting its application as identification parameter [2]. In this work, different families of human and veterinary drugs (i.e. 18 benzimidazoles, 11 5-nitroimidazoles, 11 aminoglycosides, 19 quinolones, 18 β-lactams, 10 sulfonamides and 5 tetracyclines) have been characterized in terms of mass-to-charge ratio (*m/z*) and CCS. CCS characterization has been carried out on a hybrid quadrupole-traveling wave ion mobility-time-of-flight-mass spectrometry (Q-TWIM-ToF-MS), specifically using a Synapt G2-S HDMS instrument. The developed data set includes the CCS of 173 ions considering both $[M+H]^+$ and $[M+Na]^+$ species. The main fragment ions for most compounds have also been characterized in terms of CCS. In summary, this CCS database for human and veterinary drugs includes 92 compounds of which 37 of them have been characterized in terms of CCS for the first time. CCS is a molecular characteristic closely related to *m/z*, so linear correlation between both parameters can be expected for compounds belonging to the same chemical family and with similar structural composition. High correlation between *m/z* and CCS has been observed for protonated molecules ($r = 0.9756$, $n = 91$) and sodium adducts ($r = 0.9558$, $n = 82$). As expected, CCS values for $[M+Na]^+$ are greater than for $[M+H]^+$ because they exhibit higher molecular weight. However, sodium adducts of aminoglycosides, β-lactams, and of several quinolones and benzimidazoles, present lower CCS values than expected, which involves that they are more compact ions than their related protonated molecules. Finally, 11 veterinary drugs in bovine urine samples were analyzed and no influence of the matrix on CCS values was observed, concluding to robustness of such parameter.

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P-CPA-02

DETECTION OF INTRAMUSCULAR ADMINISTRATION OF TESTOSTERONE IN CAUCASIAN AND ASIAN POPULATION USING STEROID SULFATE METABOLITES

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A liquid chromatography-tandem mass spectrometry method to quantify endogenous steroid sulfates has been used to evaluate sulfates as potential biomarkers to detect the misuse of testosterone intramuscular administration. The sample treatment consisted on a mixed-mode solid-phase extraction using WAX cartridges. Eleven endogenous steroid sulfates were included in the method, and also an estimation of three androstanediol sulfates (no commercially available) was also performed using one androstanediol sulfate which are commercially available.

The method was applied to 75 urine samples from healthy volunteers (54 males, 37 Caucasian and 17 Asian, and 21 Caucasian females) to stablish population levels of endogenous steroid sulfates in different ethnics and gender. Statistically significant differences were observed between gender for testosterone and epitestosterone sulfate, with higher concentrations in male samples. In case of ethnics, significant differences were found for etiocholanolone sulfate, with higher concentration in Asian urine samples.

Urine samples from six Caucasian and six Asian volunteers after testosterone intramuscular administration were analyzed. In addition to evaluation of sulfate concentrations, ratios between them could be also potential markers. Thus, in order to obtain the markers that are most significant in the separation between pre- and post-administration samples, principal component analysis (PCA) was used to study the sulfates and ratios. For Caucasian volunteers a separation between pre- and post-administration samples was observed in PCA, whereas for Asian no separation was observed.

Excretion profiles for each sulfate were plotted to evaluate the detection times. However, no changes were observed for the sulfate metabolite concentrations, thus they didn´t present any diagnostic power at all. In the other hand, promising results were obtained with the ratios obtained in PCA. These ratios were evaluated in all volunteers, Caucasian and Asian.

In case of Caucasian volunteers, ratios involving testosterone or epitestosterone sulfate in the denominator are the best markers, such as androsterone sulfate/testosterone sulfate (A/T) or epiandrosterone sulfate/testosterone sulfate. For Asian population the large part of ratios were not adequate markers, however for some volunteers A/T was also the best marker for the administration. Detection times for A/T were between 13 and 16 days for Caucasian, and between 10 and 15 days for Asian volunteers. The traditional testosterone/epitestosterone ratio, used nowadays to detect the EAAS misuse, allowed the detection up to 7-13 days for Caucasian volunteers, and up to 10-15 days for Asian. Thus, sulfate metabolites improved the detection capabilities, and they could be usefulness as complement markers of the steroid profile.

P-CPA-03

METABOLITE ELUCIDATION OF TWO SYNTHETIC CANNABINOIDS AFTER POOLED HUMAN HEPATOCYTES INCUBATION

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The use of new psychoactive substances (NPS) has dramatically increased in the last years. The elucidation of potential consumption biomarkers in biological fluids is necessary for the detection of drug intoxications. In this sense, *in vitro* metabolism studies using microsomes or primary hepatocytes, in combination with high resolution mass spectrometry (HRMS), has proved to be a useful approach for the study and evaluation of metabolic behaviour of NPS.

In this study, metabolites of the synthetic cannabinoids 5F-APP-PICA and AMB-FUBINACA were obtained after *in vitro* incubation with human hepatocytes. Metabolites were elucidated after analysis by liquid chromatography (UHPLC) coupled to HRMS (Q-Exactive, Thermo Scientific). Incubations were performed at 37ºC using cryopreserved human hepatocytes at 1 million viable cells/mL in Leibovitz L-15 medium supplemented with 10 % fetal bovine serum, which were individually exposed to the two synthetic cannabinoids (10 µmol/L). Cell recovery and viability was evaluated with the trypan blue exclusion method to be 71%. A blank sample was also prepared by adding vehicle to cell incubations. 20 µL of growth media were sampled after 0, 60, and 180 min of incubation for both samples and blank, and quenched with 80 µL of acetonitrile containing 100 ng/mL of 5F-Py-PICA (used as internal standard). After centrifugation, 3 µL were injected in the UHPLC-HRMS system.

The resulting Phase I metabolites of 5F-APP-PICA corresponded mainly to oxidative deamination and oxidative defluorination followed by oxidation. *N*-dealkylated metabolites were also observed. Regarding AMB-FUBINACA, the main metabolites corresponded to *O*-demethylation and *N*-dealkylation. Minor hydroxylated metabolites, including OH-indole, were also found. Regarding phase II, in both cases, the majority of metabolites corresponded to the glucuronidation of carboxylic acid moieties of Phase I metabolites.

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P-CPA-04

DEVELOPMENT, VALIDATION AND APPLICATION OF A GC-MS METHOD FOR THE SIMULTANEOUS DETECTION AND QUANTIFICATION OF NEUTRAL LIPID SPECIES IN *TRYPANOSOMA CRUZI* EPIMASTIGOTE

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Chagas disease (CD) is a chronic parasitosis caused by the protozoan *Trypanosoma cruzi* (*T. cruzi*). CD has been classified as one of the 17 neglected tropical diseases by the World Health Organization (WHO). It is estimated that around 5.7 million people are infected by CD. It causes approximately 7,000 deaths annually and is considered a serious public health problem [1].

The sterol biosynthesis pathway (SBP) is one of the most studied targets and specific metabolic pathways of *T. cruzi* that could be attacked by new drugs [2]. Sterols are a group of lipids that are constituents of cell membranes, essential for structure and functioning. Blocking SBP causes changes in the composition of the membrane, which induces defects in its ultra-structure. These changes modify the physical properties and the activity of the membrane enzymes, leading to cell lysis [3].

The development and validation of an analytical method for the simultaneous analysis of five neutral lipids in *Trypanosoma cruzi* epimastigote by GC-MS in SIM conditions is presented in this study. This analytical method has demonstrated good selectivity, accuracy, within-day precision, recovery and linearity in each of the established ranges for all the studied analytes. In addition, detection and quantification limits for squalene, cholesterol, ergosterol and lanosterol have been improved (0.31 and 0.85 µg/mL; 0.24 and 0.40 µg/mL, 0.16 and 0.75 µg/mL and 0.05 and 0.13 µg/mL, respectively) and this is the first time that squalene epoxide validation data have been reported.

This new methodology is straightforward and constitutes a tool for screening possible sterol biosynthesis pathway inhibitors in *T. cruzi*, one of the most hopeful targets in Chagas disease treatment. Therefore, it is an interesting and useful contribution to medicinal chemistry research.

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P-CPA-05

COMPARISON OF ISOTOPE PATTERN DECONVOLUTION AND CALIBRATION CURVE QUANTIFICATION METHODS FOR THE DETERMINATION OF ESTRONE AND 17β-ESTRADIOL IN HUMAN SERUM

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The estrogens estrone (E1) and 17β-estradiol (E2) are the main female sexual steroidal hormones, which are derived from cholesterol. They are involved in a high number of both gender-specific and non-gender-specific biological processes, such as growth, nervous system maturation, pregnancy and bone structure formation, in addition to their key role in breast cancer development. Therefore, there is an increasing interest in high-sensitivity measurement of these compounds in serum samples for routine analysis and clinical research.

Determination of E1 in routine analysis are usually based on radioimmunoassays (RIA), which are techniques known by the associated risks of using radioactive materials, as well as presenting bad correlation with mass-spectrometry-based methods developed more recently. Despite the expected advantages of LC-MS in terms of sensitivity and specificity, estrogens do not contain highly ionisable functional groups. That fact, together with the extremely low concentrations usually found in serum (in the range of nanogram per liter), makes necessary to resort to extensive sample treatments, expensive state-of-the-art mass spectrometers and/or even derivatization steps to include easily ionisable moieties.

In this work, we present a comparison between calibration-based and isotope pattern deconvolution (IPD) methods for the determination of E1 and E2 by LC-MS/MS, sharing the same sample treatment. Briefly, liquid-liquid extraction is applied to a small volume of serum (250 µL), the extract is then dried under vacuum, derivatized with dansyl chloride to enhance the signal in positive-mode electrospray and injected in the LC-MS/MS system. IPD, is a mathematical tool that is able to provide quantifications with a single injection. Once the distributions of abundances of natural and labelled compound are known, multiple linear regression is employed to deconvolute the resulting combined distribution in the sample spiked with internal standard, which provides the molar fractions that best fit the experimental data. Then, as the amount of labelled compound added is known, the concentration in the sample is readily obtained. As a result, IPD does not need methodological calibrations and it is regarded as a method of high metrological value, being considered in some cases as a primary method of quantification.

P-CPA-06

DETERMINATION OF SELECTED METABOLITES OF ENDOGENOUS ANDROGENIC ANABOLIC STEROIDS IN URINE BY LC-MS AND ISOTOPE PATTERN DECONVOLUTION

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Doping in sports is a current problem nowadays. Among the substances banned by the World Anti-Doping Agency (WADA), endogenous androgenic anabolic steroids (EAAS) continue to be one of the most found in positive samples. The strategy of WADA to detect the exogenous use of these substances implies the use of the individual profile of each athlete through the Athlete Biological Passport (ABP). The steroidal profile of ABP is constituted by the steroids testosterone (T), epitestosterone (E), Androsterone (A), Etiocholanolone (Etio), 5α-androstane-3α, 17β-diol (5αAdiol), 5β-androstane-3α, 17β -diol (5βAdiol) and the relationships between them [1]. Thus, the longitudinal profile based on individual references of each athlete, allows the detection of adverse analytical results.

The official method to determine steroids in urine accepted by the WADA is based on GC-MS. This method requires a previous hydrolysis of the molecules conjugated with glucuronic acid, followed by a derivatization step to convert them into volatile compounds. One way to avoid the problems associated with an extensive and tedious method, such as that method proposed by WADA, is the use of LC-MS that allows the direct injection of urine and in consequence avoids the sample treatment stages discussed above.

The present work shows the development and optimization of a method based on the simple dilution of the sample and the subsequent direct injection in a LC-MS/MS system equipped with an Electrospray source. The ionization in positive and negative mode has been tested and compared. The direct determination of the conjugated metabolites by liquid chromatography has allowed the quantification of the 5αAdiol and 5βAdiol that do not ionize in the ESI source if they are not conjugated with the glucuronic acid. The problems caused by the matrix effect have been corrected using the isotopically labeled analog compounds that have been used as an internal standard. The quantification has been carried out using the calculation methodology of Isotope Pattern Deconvolution (IPD). IPD is based on the intentional alteration of the isotopic composition of an analyte in a sample by adding an exactly known amount of the isotopically-labeled compound. The contribution of each compound (natural and labeled) to the mass spectrum of the mixture obtained experimentally, is calculated by multiple linear regression that provides the molar fraction of each of them. After that, a simple calculation provides the amount of analyte in the sample without needing to use a methodological calibration curve [2].

A part of the work done, consisted of the ionization optimization of the conjugated metabolites, the determination of the isotope pattern of the natural and the labeled compounds and the recertification of the concentration of the labeled compounds using reverse isotope dilution (RID).

Validation has been carried out in part through the use of certified reference materials and always with urine samples. The results, expected in terms of precision and accuracy for this type of methodology, are suitable for the rapid and reliable determination of selected EAAS in urine.

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P-CPA-07

APPLICABILITY OF AMBIENT IONIZATION TECHNIQUES FOR THE ANALYSIS OF DRUGS IN URINE

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The objective of doping control laboratories is to monitor the presence of different classes of substances that are prohibited in sports by the World Anti-Doping Agency (WADA). The usual strategy is to apply screening methods to find banned drugs and/or their metabolites in urine and blood. In case of positive results, laboratories have to perform a second confirmation analysis. Especially during the most important sport competitions, athlete's samples must be analyzed swiftly, being quickness of the analysis one of the main requirements for anti-doping analytical methods. Among the compounds included in the WADA prohibited list, stimulants are used to improve mental activity and to reduce physical fatigue through the stimulation of the central nervous system. For this reason, these substances are prohibited only in competition.

Currently, the most used technique for the analysis of stimulants and other WADA forbidden compounds in urine is liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). In the last few years, ambient ionization techniques, such as desorption electrospray ionization (DESI) and paper spray ionization (PS), have been extensively investigated for the determination of compounds without sample treatment or chromatographic separation. The coupling of ambient ionization with high-resolution mass spectrometry (HRMS) offers the possibility to develop very simple, fast and specific analytical methods, since the exact mass provided by high-resolution analyzers allows reducing interferences arising from sample matrix.

In this work, the applicability of DESI-HRMS and PS-HRMS is explored for the rapid and direct analysis of stimulants and other doping agents in urine. Drops of spiked urine were deposited onto different substrates and let to dry before their analysis by DESI-HRMS and PS-HRMS. For DESI-HRMS analysis, different materials, such as both porous and smooth polytetrafluoroethylene (PTFE), C18 and chromatographic paper were tested to evaluate the analyte ionization efficiency. The studied compounds generated the protonated molecule $[M+H]^+$ under both DESI and PS working conditions. In order to maximize the intensity of $[M+H]^+$, the most critical parameters were optimized (spray voltage and spray solvent composition, as well as the geometrical parameters for DESI analysis).

The comparison of obtained results showed that PS-HRMS performed better than DESI-HRMS, providing higher signal-to-noise ratios and allowing the detection of the majority of analytes at the limit of detection established by WADA without any sample treatment and with a single analysis achieved in less than 2 minutes.

P-CPA-08

FEASIBILITY OF GC-APPI-HRMS TO DETECT PHENYLALKYLAMINE STIMULANTS IN SPORTS DRUG TESTING

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Stimulants are banned during sports competitions by the World Anti-Doping Agency (WADA). The compounds selected in the study are *p*-hydroxyamphetamine, pholedrine, octopamine, norfenefrine, oxilofrine and etilefrine that are reported in the WADA list as prohibited compounds, and phenylephrine and synephrine that are currently included in the Monitoring Program [1]. These hydroxylated phenylalkylamines include isomers that are difficult to retain and separate by reversed-phase liquid chromatography (LC). Due to the low volatility of target compounds, a derivatization step is required before their analysis by gas chromatography (GC), being trimethylsilyl (TMS) and trifluoroacetil (TFA) derivatives the most frequently used. The ionization of these stimulants by electron ionization mass spectrometry (EI-MS) yields highly fragmented spectra, which leads to the loss of selectivity in their determination in anti-doping analysis. Atmospheric Pressure Photoionization (APPI) is a soft ionization source, normally used in LC-MS, that maximizes molecular ions providing low in-source fragmentation. Recently, the development of a new GC-APPI interphase has expanded the applicability of APPI to new fields. In this work, a GC-APPI-HRMS method was investigated for the analysis of the eight aforementioned stimulants in urine samples. Two derivatization reactions were studied: the formation of TMS derivatives with N-methyl-N-trimethylsilyl trifluoroacetamide (MSTFA) and the formation of TMS/TFA derivatives with MSTFA and N-methyl-bis(trifluoroacetamide) (MBTFA) as derivatization reagents. The best chromatographic separation of the derivatized compounds was achieved using a 100% dimethylsiloxane capillary column and their determination was performed using a quadrupole-Orbitrap mass spectrometer, which operates at ultra-high-resolution (70,000 FWHM, *m/z* 200) in positive ion detection mode. Among the solvents tested as dopant agents, acetone provided the best results yielding the protonated molecule $[M+H]^+$ and a very low in-source fragmentation. The intensity of $[M+H]^+$ was maximized by optimizing the most critical APPI parameters: dopant flow rate, s-lens and source temperature. At the optimal working conditions, the methods for both derivatives allowed the detection of $[M+H]^+$ and two in-source collision-induced dissociation (CID) ions for most analytes, fulfilling the identification requirements in doping analysis. A characteristic in-source CID fragmentation pattern was observed depending on the structure of the analytes. Urine samples were analyzed by GC-APPI-HRMS after solid-phase extraction with Bond-Elut certify cartridges. Compared with GC-EI-MS, the developed GC-APPI-HRMS method provided lower detection limits and improved selectivity.

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P-CPA-09

TOWARDS AN ENHANCED CHEMICAL STABILITY AND BIOAVAILABILITY OF CAMPTOTHECIN THROUGH THE FORMATION OF CICLODEXTRIN INCLUSION COMPLEXES. A RP-HPLC-FL EVALUATION

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The use of cyclodextrins (CDs) as drug nanocarriers to act as delivery systems, enhance their stability [1] and solubility [2], and also to mask their side effects, is gaining importance in pharmaceutical industry. These glucose oligomers have been accredited as “generally recognized as safe” by FDA and they are commonly employed in different pharmaceutical dosage forms.

Camptothecin (CPT) is the lead compound in a family of clinically relevant topoisomerase 1 inhibitors with potent anti-cancer activity but, due to its rapid inactivation at physiological pH, requires the development of methods to contribute to its chemical stabilization. The formation of inclusion complexes with CDs can provide an elegant way to achieve this goal.

In this context, we have prepared the inclusion complexes of CPT with beta-CD and 2-hydroxypropyl-beta-CD. The complexes were isolated and characterized by ^{1}H-NMR. The efficiency of the complexation was verified by UV-Vis spectrophotometry because the protonation equilibrium of CPT was drastically hampered for the inclusion complexes. With the aim of confirm the stabilization of the CPT-CD inclusion complexes, the quantitation of the active lactone form was carried out by RP-HPLC with fluorimetric detection, using luotonin A as the inner standard. In alkaline solution (pH = 9.0-10.0), 59.8 % of the CPT lactone was hydrolyzed into the corresponding hydroxy acid form after 15 min at 25 °C, while under the same experimental conditions an 80 % of lactone remained unchanged in the presence of beta-CD. The stability of the isolated solid CD inclusion complexes was higher, with 96 % and 93% of the lactone form remaining for beta-CD and HP-beta-CD inclusion complexes, respectively. The pharmacological assays for the complexes also showed enhanced activity, probably due to an improved drug solubilization.

Acknowledgments: Financial support from MINECO (grant CTQ2015-68380-R) is gratefully acknowledged.

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P-CPA-10

IONIC LIQUIDS AS MOBILE PHASE ADDITIVES FOR ENHANCING THE SEPARATION OF ANTICANCER DRUGS BY HPLC WITH FLUORIMETRIC DETECTION

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Camptothecin (CPT) is a natural product that was first isolated in 1966 from the bark of *Camptotheca acuminata*. CPT and its analogues constitute the main family of clinically relevant topoisomerase I inhibitors [1,2]. The lactone group in CPT is essential for the stabilization of the CPT-DNA-topoisomerase tertiary complex, but it leads to a low chemical stability and to the existence of two CPT species, namely the lactone and hydroxy acid forms. The quantitation of both forms by HPLC requires gradient elution, or isocratic elution with tetrabutylammonium phosphate as mobile phase modifiers.

Ionic liquids (ILs) have been applied as mobile phase additives in HPLC [3] to enhance the chromatographic behaviour of a variety of analytes with acid or basic character. ILs behave as an effective umbrella for unencapped silanol groups and they provide enhanced peak profiles, decrease peak tailing and peak broadening and thus, they improve analysis time, efficiency and resolution.

In the present communication we describe the benefits derived from the use of ILs for the chromatographic separation of CPT lactone and hydroxy acid as well as the structurally related anticancer agent luotonin A. 1-Butyl-3-methyl-imidazolium chloride and 1-butyl-1-methyl-pyrrolidinium chloride were tested as mobile phase additives. Acetonitrile:water 40:60 mobile phases containing increasing amounts (0-50 mM) of these imidazolium and pyrrolidinium derivatives were tested. The aqueous component of the mobile phase was buffered at pH 3.0-3.5. Under these experimental conditions, the retention factor and selectivity were increased in the presence of both ILs. The number of plates (*N*) was significantly increased in the presence of the pyrrolidinium salt in comparison to the imidazolium chloride, but for both ILs, the efficiency was increased. Furthermore, the addition to ILs to the mobile phases allows the separation of the hydroxy acid and lactone forms of CPT under isocratic elution. The use of luotonin A as an inner standard facilitates the quantitation of both CPT forms at different pH values.

Acknowledgments: Financial support from MINECO (grant CTQ2015-68380-R) is gratefully acknowledged.

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P-CPA-11

BIOACCUMULATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN HUMANS. DIFFERENTIATION BETWEEN ORGANS USING MULTIVARIATE DISCRIMINANT ANALYSIS

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Polycyclic aromatic hydrocarbons (PAHs) represent a class of over 200 different chemicals containing two or more aromatic rings. These contaminants are extensively distributed in aquatic habitats, as well as in air, soils, flora and fauna. PAH exposition mainly occurs by air inhalation, food ingestion [1] or through skin, due to its high permeation for protein-lipid, being then accumulated in the fatty tissue of the body or mammary glands [2]. Fish tissues are the biological matrices more studied for their PAHs quantification; nevertheless, the literature dealing with other animal or human tissues is scarce [3].

The bioaccumulation of thirteen polycyclic aromatic hydrocarbons (PAHs) in humans was studied, using seven organ tissues (brain, lung, kidney, liver, heart, fat and spleen) obtained through eight autopsies. The contaminants were prior isolated from the tissues by using a salting out liquid extraction with acetonitrile. Due to the low concentrations of these compounds in the human body, a dispersive liquid-liquid microextraction (DLLME) procedure was included in the sample treatment using the acetonitrile extract. The preconcentrated samples were analyzed by gas chromatography-mass spectrometry (GC-MS). The quantification limits were in the 0.06-0.44 ng g^{-1} range, depending of the compound, and a mean intraday relative standard deviation of about 7% demonstrated a high precision. As far as we know, this methodology has not been applied for PAHs determination in human organs from autopsies.

Seven different tissues for eight autopsies were analyzed and the PAHs contents were submitted to statistical analyses. An ANOVA test was applied to study the tendency of the different organs to bioaccumulate PAHs and, also, to distinguish which compounds were found at higher concentrations in each organ. The results were confirmed by a principal component analysis (PCA) to show the natural clustering of samples between group autopsies using the individual concentration of each PAH, the score plot demonstrating no separation between groups. Moreover, an orthogonal partial least square discriminant analysis (OPLS-DA) was applied to the data to build a multivariate regression method which permitted the classification of autopsies considering age and sex.

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P-CPA-12

DETERMINATION OF NUCLEOTIDES IN SUPPLEMENT FEED USING ION-PAIR LIQUID CHROMATOGRAPHY WITH DUAL ELECTROSPRAY ATMOSPHERIC PRESSURE CHEMICAL IONIZATION TIME-OF-FLIGHT MASS SPECTROMETRY

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Health care is nowadays of great importance for both farm animals and pets. With this purpose, different balanced concentrates of free nucleotides and active precursors are commercialized, most of them obtained from yeasts. In earlier steps of life, animals suffer many stress situations, and an ideal diet can make the difference between a healthy start and a difficult one. The multiple functions attributed to nucleotides, such as immune-, lipidic- and digestive-related, have led to their use in animal feed. Nucleotides are also indicated for immunosuppressed or convalescent animals, as well as for those which support situations of sport stress.

The use of a sensitive procedure the determination of the five permitted nucleotides [1]: cytidine 5´-monophosphate (CMP), uridine 5´-monophosphate (UMP), adenosine 5´-monosphosphate (AMP), guanosine 5´-monophosphate (GMP) and inosine 5´-monophosphate (IMP), in supplement feed for animals is proposed. Ion-pair liquid chromatography (IP-LC) with dual electrospray atmospheric pressure chemical ionization (ESI-APCI) for time-of-flight mass spectrometry (TOF-MS) is used [2]. N,N-dimethylhexylamine was used as the ion-pair reagent at 5 mM concentration in the mobile phase, also improving the compatibility of LC with ESI-APCI. The samples analyzed, commercialized as palatable tablets and powders, are recommended for use in piglets and immunocompromised dogs and cats. Under the finally selected conditions, 25 mg of sample were homogenized with 2 mL of water and then 1 mL 3% m/v trichloroacetic acid was added. The mixture was left to stand for 15 min to allow precipitation of the proteins and the supernatant obtained after centrifugation was filtered and diluted up to 5 mL with water. Aliquots of 20 µL were injected into the LC system. Calibration against aqueous standards was used for quantification purposes. Detection limits between 0.3 and 0.5 µg mL^{-1} (57-98 µg g^{-1}) were obtained, depending on the compound. Intra-day RSD values in the 4-11% range was obtained. The selectivity of the method was provided by the power of high resolution and accurate mass measurements of LC-TOF-MS. The errors obtained were between -1.72 and 2.62 ppm, being in all cases lower than the accepted accuracy threshold of 5 ppm for confirming elementary composition.

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P-CPA-13

SEPARATION AND IDENTIFICATION BY (RP)UHPLC-UV-MS OF FOUR THERAPEUTICAL MONOCLONAL ANTIBODIES

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The use of therapeutic monoclonal antibodies (mAbs) in clinical practice is well established nowadays. They are widely used in hospitals for the treatment of highly prevalent illnesses such as cancer and auto-immune diseases. Usually therapeutic mAbs are supplied to the patients individually, however it has been reported that in some cases a combination of mAbs could have a greater therapeutic potential than a single mAb. This implies that the use of mAb combination in cancer therapy is becoming a promising in the near future. In this context, it is important to provide rigorous and reliable analytical methods that enable us to resolve mixtures of mAbs and determinate each one.

mAbs are composed of four peptide chains, two light (L) and two heavy (H) ones, stabilized by inter-chain disulphide bonds. Both H-chains and L-chains contain variable and constant regions. The variable regions, which are the antigen-binding site of the antibody, display different specificities and differ in the amino acid sequence between mAbs. In the light of the above all mAbs share the same IgG1 structure, differing only in the region involved in specific interaction with the antigen. This structural similarity difficult the separation of mixtures of mAbs by reversed phase (RP) chromatography.

In this communication we present a novel and straightforward (RP)UHPLC method for the separation of a mixtures of the four widely used mAbs: bevacizumab (BVZ), cetuximab (CTX), infliximab (INF) and rituximab (RTX) in mixtures. A (HESI/Orbitrap)MS system coupled to the chromatographic equipment was used to properly identify each one. In addition, the method was validated for quantification using the signal from the UV spectrophotometric detector. Performance parameters such as linearity, accuracy (precision and trueness), detection limits, quantification limits and robustness were evaluated. Robustness was established by studying both total and one-sided effects of four selected variables: column temperature, modifier (trifluoroacetic acid) content in the mobile phases, initial proportion of eluent B and gradient slope. The isoform profile of each mAbs was also obtained in order to identify by mass each mAbs. The results indicated the suitability of this analytical method for resolving and singly quantifying these four mAbs.

P-CPA-14

NATIVE MASS SPECTROMETRIC SIZE EXCLUSION LIQUID CHROMATOGRAPHIC ANALYSIS OF THE MONOCLONAL ANTIBODIES INFLIXIMAB AND BIOSIMILAR CT-P13: AGGREGATES AND INTACT ISOFORMS PROFILES

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Monoclonal antibodies (mAbs) represent actually an important class of biopharmaceutic, they have proved enormously success in the treatment of cancers and autoimmune diseases, both widespread disease. Infliximab (INF), the active pharmaceutical ingredient (API) of the world wide used medicine Remicade®. INF is indicated for the treatments of rheumatoid arthritis, Crohn's disease, etc. CT-P13, the biosimilar of INF, is the API of the medicine Remsina® and Inflectra®.

The dynamic nature of the structure of mAbs, typical of proteins, leads to a natural tendency to form aggregates. In solution, the exposition of the internal hydrophobic amino acid residues to the aqueous medium promotes the interaction with other protein entities forming higher order aggregation. Aggregation process represents severe problems in biopharmaceutics due to the induced immunologic response in patients. Therefore, as aggregation can affect a therapeutic mAb at any stage of its life, from its development and production to its final intravenous administration to the patient in solution, it is important to control this process throughout all this period.

Size exclusion liquid chromatography (SE)LC or simply SEC, is the most commonly used method to separate and quantify mAbs aggregates. The main advantage is its high sensitivity to distinguish monomers from dimers and from fragments with high efficiency, repeatability and robustness. SEC is also considered a native analytical method of proteins. Traditionally, the mobile phase compositions required in SEC (pH 7 buffer solutions with no organic solvent) is not suitable for coupling to mass spectrometric detection. Recent development of new SEC columns allows using mobile phases which no suppress the mAb ionization, called "native mass spectrometry" (SEC-(native)MS). In very recent years, several papers have been published demonstrating the applicability of native MS for the qualitative and quantitative aggregates characterization of mAbs and new therapeutic protein formats [1].

In this study, we present the development of a (SE)UHPLC-UV- native MS method for the detection of aggregates in formulations of INF and its biosimilar CT-P13. In addition, intact isoform profiles in native mode were obtained and identified.

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P-CPA-15

IS STRONGER ALWAYS BETTER? EFFECT OF URINE FREEZING TEMPERATURE ON PROSTATE SPECIFIC ANTIGEN (PSA) ANALYSIS BY CAPILLARY ELECTROPHORESIS IN THE SEARCH OF PROSTATE CANCER MARKERS.

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The need of new more selective prostate cancer markers is worldwide accepted. In our group, changes in glycosylation of proteins, and namely of the prostate specific antigen (PSA), related to prostate cancer are investigated. Taking into account the problems to obtain PSA from other fluids, urine has been our choice to be investigated as PSA source.

Along previous studies performed in our laboratory to analyze PSA from urine, degradation or loss of the glycoprotein in the natural samples has been observed. Choosing the storage conditions for urine samples is not trivial and it is a non-solved problem in urine banks. In addition, the optimal conditions are very dependent on the analyte to be determined.

In the present study the effect of storage conditions on the capillary electrophoresis (CE) profile of PSA is studied using a pool of urine samples.

PSA is purified from urine by affinity chromatography using in-house made mini-HPLC columns. Alterations in PSA glycosylation are monitored by changes in the CE profile of the intact glycoprotein using the method developed in our laboratory [2].

To perform the study, it is taken into account that the samples are stored during two periods. First, urine is stored from the collection until it is purified to obtain PSA from it. And second, the PSA purified is stored until the CE analysis is performed.

The results of this study indicate that higher recovery is obtained for storage of both, the urine and the purified PSA, frozen at -20 ^{o}C than at -80 ^{o}C.

By controlling that the urine does not show infection and by freezing the samples, not disturbed CE profiles of PSA were obtained.

This work allows to establish the storage conditions to make possible the ulterior study of PSA alterations related to prostate cancer using a large number of urine samples.

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P-CPA-16

CAPILLARY ELECTROPHORESIS IN COMBINATION WITH FIELD AMPLIFIED SAMPLE INJECTION FOR THE DETERMINATION OF TETRACYCLINES IN HUMAN URINE SAMPLES

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Tetracyclines (TCs) are one of the primarily antibiotic groups used for veterinary purposes and human therapy. Considering that urine samples are easier to collect than other biological materials, such as blood or tissues, fast and simple methods are needed for the screening or quantitative determination of drugs, to adjust the therapeutic doses or in pharmacokinetic studies. In this presentation, a sensitive method using capillary zone electrophoresis with UV detection has been developed for the determination of five TC antibiotics (oxytetracycline, methacycline, tetracycline, chlortetracycline and doxycycline) in human urine samples. The electrophoretic separation was achieved using a voltage of 20 kV (normal mode). The background electrolite was an aqueous solution of 75 mM sodium carbonate and 1 mM EDTA adjusted to pH 10.0 with 1 M NaOH. The temperature of the capillary was kept constant at 25°C. TCs were monitored at 270 nm. To improve the sensitivity of the method, an on-line preconcentration strategy, named field-amplified sample injection (FASI) has been studied. FASI is a very and simple preconcentration technique that only requires the electrokinetic injection of the sample after the introduction of a short plug of a high-resistivity solvent, achieving high enhancement factors. Parameters affecting the performance of the FASI procedure, such as sample solvent composition and injection time, among others, were optimized. Under optimum conditions, sensitivity enhancement factors ranged from 450 to 800 for the studied compounds. Taking into account the range of the concentrations usually found in human urine samples from patients under treatment with TCs (1.5–200 mg L^{-1}), the enhancement in sensitivity achieved using FASI as on-line preconcentration allowed to apply directly the “dilute-and-shoot” (DS) procedure. DS consisted of diluting the sample with the solvent (1:1000) as unique step, reducing the influence of the matrix in the on-line preconcentration step and simplifying the method.

The applicability of the proposed method was demonstrated by the determination of these antibiotics in spiked urine samples. The limits of quantification were lower than 0.8 mg L^{-1} and the precision (intra- and inter-day), expressed as relative standard deviation (%RSD) was below 14%. Recoveries ranged from 92.1 to 96.7%. Thus, the proposed procedure is a simple, fast and efficient strategy, which could be used as therapeutic drug monitoring in human urine samples.

P-CPA-17

DETERMINATION OF SYNTHETIC CATHINONES IN URINE BY SOLID-PHASE EXTRACTION FOLLOWED BY LIQUID CHROMATOGRAPHY-HIGH RESOLUTION MASS SPECTROMETRY

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In recent years, the consumption of new psychoactive substances has increased considerably. Among the different substances included in this group, cathinone derivates have become very popular as legal highs. Moreover, these substances are easily obtained in the market as "bath salts", avoiding the legislation due to their modified structure based on banned substances [1]. Once synthetic cathinones are taken, they are absorbed in the tissues and since they are lipid soluble, they are metabolized in the liver prior elimination through urine. Until now, different methods have been developed to determine trace levels of cathinones in environmental and biological samples. These methods are based on solid-phase extraction (SPE), using different types of sorbents followed by liquid chromatography (LC) with tandem mass spectrometry, or high resolution mass spectrometry (HRMS) in very few cases [2-4].

The aim of the present study is to develop and validate a method for the determination of a group of eleven trending synthetic cathinones in urine using SPE followed by LC-HRMS using Orbitrap as analyzer.

In the extraction step, two different cation-exchange sorbents have been evaluated, a weak (Oasis WCX) and a strong one (Oasis MCX) [4]. Better results were obtained for Oasis MCX in terms of recoveries (around 100%) and matrix effects (lower if a clean-up step was applied). Hence, although a matrix-matched calibration curve was necessary, the matrix effect was reduced considerably. Repeatability and reproducibility values, in terms of relative standard deviation (%RSD), were lower than 13% in urine samples. The linearity was between 0.2 ng mL^{-1} and 100 ng mL^{-1} for most compounds and 0.2 ng mL^{-1} and 150 ng mL^{-1} for five of them. Method quantification limits were set at 0.2 ng mL^{-1} and method detection limits were between 0.04 ng mL^{-1} and 0.16 ng mL^{-1}, enabling the quantification of the studied compounds at the usual levels at which they are present in urine samples [5].

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P-CPA-18

BIOASSAY-GUIDED ISOLATION OF ANTI-OBESITY POLYPHENOLS FROM *LIPPIA CITRIODORA*

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Lippia citriodora (lemon verbena), a shrub indigenous to South America, was introduced into Europe at the end of the 17th century and has been widely used in infusions for its antispasmodic, antipyretic, sedative, and digestive properties. Furthermore, this plant is used in the food industry to flavor different products. Lemon verbena infusion contains significant amounts of polyphenols with healthy properties including high antioxidant activity [1].
Recently, the relationship between nutrients and health is becoming since natural dietary products as polyphenols are being considered by their potential for the management of several diseases. Nevertheless, a better knowledge of the phenolic composition from lemon verbena polyphenols could be useful for nutraceutical development.
We aimed to investigate the capacity of *Lippia citriodora* compounds to modulate AMP-activated protein kinase activity (AMPK) on a hypertrophic adipocyte model. HPLC semi-preparative purification method and reverse phase high performance liquid chromatography coupled to time-of-flight mass detection with electrospray ionization (RP-HPLC-ESI-TOF/MS) [2] were used to obtain de compounds from *L. citriodora* extract. AMPK activity was measured on the hypertrophic 3T3-L1 adipocyte model by immunofluorescence microscopy.
Four compounds of 29 total compounds have been tentatively identified in *L. citriodora* for the first time by HPLC-ESI-TOF-MS. Phenylpropanoids (verbascoside), iridoids (gardoside) and flavonoids (luteolin-7-diglucoronide) were the best candidates to account for activating AMPK capacity.
The combination of specific polyphenols from *L. citriodora,* which showed strong activating AMPK capacity, could be an alternative in the management of obesity-associated diseases.

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P-CPA-19

ANALYTICAL CHALLENGES ASSOCIATED TO THE CONTROL OF FASHION COSMETICS SAFETY

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Cosmetics, which include all personal care and hygiene products [1], are one of the main pillars of current consumption and are used daily by the population. One of the big analytical challenges associated with the regulatory control of these products is related to cosmetics of new format or those considered as *borderline* products. In this context tattoos stand out, both permanent and temporary. Their safety and regulation are recently important issues [2], in particular with regard to their main ingredients, the colorants. Tattoo colorants are now based on modern-pigment chemistry, but there is no systematic surveillance on their safety. These ingredients are synthetic and organic hydro- or liposoluble compounds, and this wide range of solubilities makes joint analysis difficult. Most of them are unstable but little is known about the degradation products, so the analysis of their photochemical stability is also fundamental from several points of view: shelf life of the product, risk to the consumer and environmental fate.

Therefore, it is necessary to develop appropriate methodologies (sample preparation and analytical determination using chromatographic techniques) for the analysis of these complex samples; and also to evaluate the stability of selected ingredients in solution, in real cosmetic matrices and "in vitro" systems.

This work shows the first experimental tests carried out. On the one hand, a study of the photo stability of a pigment present in most of the transferable picture tattoos [3], Lithol Rubin BK. For the constant and continuous irradiation of the samples, a solar radiation simulator was used, Suntest CPS +. On the other hand, the characterization of a set of inks for permanent tattoos purchased on a well-known website and available to anyone. In both cases, samples are analyzed by liquid chromatography with DAD and MS / MS detectors.

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P-EA-01

VALIDATION STUDY OF AN ON-LINE ANALIZER FOR THE DETERMINATION OF TRIHALOMETHANES IN DISTRIBUTION DRINKING WATER ACCORDING TO ISO 17025

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During the water disinfection treatment, a group of by-products compounds called trihalomethanes (THMs) are produced by the reaction between the organic matter present in treated water and chlorine. Over the years, several studies have proved their potential carcinogenicity which has made mandatory to regulate their concentration in drinking water. In particular, the European Directive 98/83/CE stablishes a mandatory limit of 100µg/L for the sum of the four THMs for consumption water.

The use of on-line analysers along the net water distribution allows a better optimization of the management distribution water quality system. The analyser AMS-ATM-100 is an instrument manufactured by Aqua Metrology Systems (USA), based on purge and trap techniques, a Fujiwara's reaction and spectrophotometric detection for the analysis of THM. Extraction and concentration of volatile analytes take place in a Carbopack/Carbopxen trap, followed by a thermal desorption, a modified Fujiwara reaction and a spectrophotometric detection at 540nm that allows to quantify and monitor the concentration of total and individual trihalomethanes.

The validation study was performed in three stages focusing on ISO 17025 requirements. Firstly, an on-line study was performed with distribution's water in the laboratory, with accuracy's results for THMs between 18% and 12% considering two types of speciation. Secondly, an off-line study with spiked quality control samples was carried out considering these two types of speciation as well. Accuracies of -7,6-3,5%, precision of 4,6-5,8% and uncertainties of 12-19% were obtained at 20µg/L for THMs and at 120µg/L -4,8- -8,5% of accuracy, 2,3-3,9% of precision and 12-18% of uncertainty. Validation of instruments installed in four different sites in the distribution system, was accomplished with spiked quality control samples with resulting precision for THMs between 3,9-6,3% at 46µg/L and 2,7-6,9% at 12µg/L and uncertainties' results for THMs showed values between 8,0-18% at 46µg/L and 5,9-26,6% at 12µg/L.

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P-EA-02

DIRECT DETERMINATION OF ULTRATRACE TOTAL INORGANIC IODINE IN SEAWATER BY LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY

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Iodine is a ubiquitous element that can be found widespread in living organisms, Earth's crust, atmosphere, and especially, seawater. Atmospheric iodine plays a relevant role in climate change, modifying the oxidative capacity of the troposphere through a number of processes, including the depletion of ozone by catalytic cycles. Bearing in mind that most of this iodine comes from the oceans, analytical methods capable of detecting and quantifying iodine in seawater are necessary. However, this is a challenging matrix because iodine species (iodide and iodate) concentration extends over several orders of magnitude and high concentrations of other anions and cations are also present. These facts make difficult to get reliable values with most of common analytical methodologies.

In this work, the first method capable of the direct determination of total inorganic iodine at subnanomolar level based on liquid chromatography-electrospray ionization-mass spectrometry (LC-ESI-MS) without any sample treatment is presented. The chromatographic method has been developed using a bimodal LC column, and optimized applying a Response Surface Methodology based on a Box-Wilson Central Composite experimental design. The MS detection was carried out by ESI in the negative ion mode, monitoring the *m/z* 127.

Analytical characteristics of the developed method were studied in terms of linear range, limit of detection, instrumental precision (repeatability and intermediate precision), and robustness. The matrix effect was also estimated comparing the slopes of calibration curves made in Milli-Q and simulated seawater. The instrumental detection limit for iodide was as low as 0.25 nM, injecting 5 µL of seawater without any treatment and the working linear range obtained (up to 250 nM) was wide enough to cover the broad concentration range observed in seawater samples. Average values for repeatability and intermediate precision were 4.0% and 6.9%, respectively. The suitability of the method was demonstrated through its application to the analysis of several seawater samples taken at different locations along the Spanish Mediterranean coast and some domestic iodized salts.

According to the results obtained, the method developed is rapid, easy to apply, avoids sample treatment and requires only a few microliters of sample. Furthermore, its low detection limit allows the quantification of inorganic iodine in seawater from any location and depth.

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P-EA-03

CHARACTERIZATION OF THE ORGANOHALOGENATED BURDEN IN INFERTILE *MILVUS MIGRANS* EGGS FROM A CONTAMINATED AREA IN MADRID (SPAIN)

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Targeted environmental monitoring reveals contamination by known chemicals, but may exclude potentially pervasive but unknown compounds [1].

This study evaluates the potential of comprehensive two-dimensional gas chromatography coupled to a time-of-flight mass spectrometry (GC×GC-ToF MS) for the non-targeted characterization of the halogen-containing micropollutants present in infertile black kite (*Milvus migrans)* eggs subjected to a simplified and generic sample preparation treatment [2]. Eggs (10 samples) were collected from a black kite population nesting in a heavily polluted area near to Madrid. Two sampling periods were considered, 2007-08 and 2015-16. GC×GC-ToF MS analysis of the extracts were performed under previously optimized conditions [3]. Generated data were automatically filtered for chloro-, bromo- and mixed chloro-bromo-containing analytes by using a previously optimized script function [3].

In total, 104 halogen-containing compounds were either positively or tentatively identified in the investigated samples. Although the number of compounds varied depending of the investigated sample (from 66 to 85), in all cases, the main classes contributing to the total organohalogenated burden were the polychlorinated biphenyls (PCBs), polybromodiphenyl ethers (PBDEs) and different organochlorinated pesticides. Among these, PCBs were the most numerous family with 82 analytes. Other micropollutants, such as chlorobenzene- and methylbipyrrole-derivatives, were minor contributors also identified in the investigated eggs.

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P-EA-04

MULTI-RESIDUE ANALYSIS OF 22 CONTAMINANTS OF EMERGING CONCERN IN RIVER WATER BY LARGE VOLUME DIRECT INJECTION-LIQUID CHROMATOGRAPHY TANDEM MASS SPECTROMETRY

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Although contaminants of emerging concern (CECs) are generally found in the aquatic environment at the trace level, the continued release and subsequent exposure of the aquatic media to these pollutants has awakened great concern, especially when water is used as a source for drinking water production. As a consequence, strict regulations have been established to control the presence of CECs in the aquatic ecosystems [1, 2].

Currently high-throughput multi-residue analytical methods for determining CECs in environmental waters are required, which usually include sample preparation procedures based on off-line solid–phase extraction (SPE) [3]. However, fully-automated methods based on on-line SPE coupled to liquid chromatography tandem mass spectrometry (LC-MS/MS) are preferred for routine laboratories which need to analyze a large number of samples [4]. Recently, with the use of modern and sensitive mass analyzers, the direct injection of large sample volumes (LVI) has been applied in several studies as a rapid and efficient alternative approach for the determination of CECs in water samples [5].

This study describes the development of a multi-residue method based on LVI coupled to LC-MS/MS for the determination of 22 CECs belonging to different classes (pesticides, pharmaceuticals and personal care products) in surface water. The precision of the method, calculated as relative standard deviation (RSD) (n=5, at 25 and 250 ng L^{-1}) was below 19% for all compounds. The limits of quantification (LOQs) were between 0.5 and 5 ng L^{-1} for most of the compounds studied.

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P-EA-05

ACT MICROPLASTICS AS CONCENTRATORS OF ORGANIC POLLUTANTS SUSPENDED IN WATER? FOR EXAMPLE, PBDEs

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Pollution by plastic debris in the oceans is an increasing environmental concern because with the pass of the years the plastics are degraded giving small sized particles. Micrometer sized plastics (500 µm to few micrometers) are numerically abundant and widespread across the world's ocean surface [1].

The main concern is that the fragments of plastics could contain pollutants, such as polybrominated diphenyl ethers (PBDEs), coming from the manufacture or adsorbed from sea water through sorption processes. As the size of microplastics is similar to plankton size, marine organisms do not difference between the two of them during their alimentation and introduce them into the trophic chain [2][3].

Therefore, the goal of this project is to demonstrate the adsorption of PBDEs on the most common used microplastics (PET, PP, PS and PE). We determined the amount of pollutant adsorbed to the different type of microplastics and the structure-related differences in its absorption using the gas chromatography technique coupled to an electron capture detector (GC-ECD). Using a 5 m column and the splitless mode we can analyze 14 of the most common studied PBDE compounds in 42 minutes. Moreover, with the electron capture detector, a specific detector used for the analysis of halogenated compounds we can reach the sensibility and selectivity that we need for the concentrations that we are working with.

This study will be applied to samples collected (filters with microplastics retained) during the Barcelona World Race 2015 from different points of the oceans where the regatta boat sails, giving evidence of the concerns associated with the presence of microplastics in the seawater and which is the level of pollution for the different oceans of study.

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P-EA-06

DIRECT DETERMINATION OF POLYCHLORINATED BIPHENYLS IN SOLID AND SEDIMENTS BY THERMAL DESORPTION-GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Polychlorinated biphenyls (PCBs) are ubiquitous organic pollutants often present in environmental samples due to their physical and chemical stability. PCBs family include 209 congeners, but only seven indicator congeners (28, 52, 101, 118, 138, 153, and 180) are typically measured for environmental studies like soils and sediments. Methods for the extraction of PCBs from soils are typically based in the use of Soxhlet and sonication conventional methods, and an assorted number of high performance extraction methods based in the use of supercritical fluids, pressurized solvent or microwaves. Those extraction methods also provide a co-extraction of high amounts of matrix compounds; so, an intensive clean-up of extracts is imperative before chromatography separation. As results, PCBs analysis typically involves long and tedious procedures (several hours) and high reagent and solvent consumption. Thus, in this study the use of thermal desorption-gas chromatography-mass spectrometry (HS-GC-MS) was proposed for the direct determination of PCBs in soils and sediments. All samples were stored in a freezer at -8 °C and freeze dried before PCB analysis. Then, 20 mg were accurately weighted in a glass thermal desorption tube between two glass wood pieces and directly analyzed by HS-GC-MS, without any additional sample treatment. TD was carried out at 265 °C for 20 minutes, and analytes were trapped in an internal Tenax trap at -10 °C. A second desorption was carried out at 10 °C s^{-1} till 275 °C and PCBs were directly introduced in the GC-MS system. The procedure can be automatically programmed in order to perform the extraction step during the acquisition of the previous chromatogram. Thus, extraction time can be assumed to be zero and as consequence the limiting step was the chromatography analysis. Different parameters were evaluated such as: soil amount and type of soil. The proposed HS-GC-MS methodology reach limits of detection between 0.40 and 0.98 ng g^{-1} PCBs and appropriate precision values with relative standard deviation lower than 15 %. Recoveries were assessed using soil and sediment samples spiked with PCBs at 5 and 50 ng g^{-1} and also by using certified reference material IAEA357 marine sediment homogenate, providing quantitative recoveries. Thus, to conclude, a tremendously fast method was proposed for the analysis of PCBs by HS-GC-MS, avoiding any sample treatment and enough sensitivity to discriminate contaminated soil and sediment areas.

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P-EA-07

BIOFERTILIZATION OF VINEYARDS: INFLUENCE OF VERMICOMPOST IN THE POLYPHENOLIC PROFILE OF GALICIAN WINES

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Grape marc is a winery residue generated in large amounts in regions such as Galicia, and its accumulation is an important environmental and economical problem. This organic vitivinicultural waste is a source of bioactive polyphenols [1] interesting for industrial applications in cosmetics, pharmacy and food. Another new application can be as organic amendment in agriculture, with a previous treatment to decrease the high polyphenolic concentrations that can inhibit the growth of roots [2] and plants. The possible application of vermicomposting as an alternative for the treatment and reuse of this type of waste [3] shows a practical scheme of circular economy.

Using the grape marc (white and red) from two Galician wineries as raw material, a vermicomposting process were carried out in order to obtain a stable and quality vermicompost to use as biofertilizer in the own vineyards, with the purpose of achieving differentiated Galician wines. The final objective is obtaining two Galician natural wines (white and red) from vines fertilized with vermicompost and compare them to the typical wines (control wines) in which this biofertilizer was not used. To do this, the polyphenolic content of wines were characterized using chromatographic techniques in combination with other spectrometric ones as support. High efficiency liquid chromatography with diode array detection (HPLC-DAD) was used for the determination of the individual polyphenolic profiles and the quantitative analysis. The main polyphenols detected in the wine samples were the phenolic acids gallic and caftaric in *whites* and the anthocyanin malvidin in *reds*.

This is a three-year project, and in this work, we are showing the results corresponding to the first harvest, where natural wines and control wines showed similar polyphenolic profiles, without significant differences. Nevertheless, an expert panel has already detected organoleptic differences, and hence we are also working in the aromatic profile (GC-MS) in order to find the chemical source of these differences.

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P-EA-08

IDA AND SWATH AS NON-TARGET ACQUISITION TECHNIQUES TO IDENTIFY PHARMACEUTICALS IN COMPLEX ENVIRONMENTAL MATRICES

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The utilization of non-target screening provides the opportunity to expand the knowledge on low-molecular-weight organic pollutants present in environmental matrices through suspected or non-target screening. However, one of the pending issues that still remains is the number of compounds properly identified (with some fragment ions). To solve this problem, new instrumental acquisition methods are being developed. In this study, liquid chromatography-quadrupole time-of-flight mass spectrometry (LC-QqTOF-MS) using suspected screening have been applied to mussels (*Mytilus galloprovincialis*) and riverine sediments of the Turia River Basin, in Eastern Spain. The extraction of the sediment was carried out by ultrasound assisted extraction (UAE) with McIlvaine buffer (pH 5.4) and methanol. Then, extracts were cleaned up by solid phase extraction (SPE) with Strata^{TM}X cartridges and retained analytes were eluted using methanol-dichloromethane. In the case of mussels QuEChERS was selected as extraction procedure using a mixture of Acetonitrile, water, $MgSO_4$, NaCl, $2Na_2C_6H_6O_7$ and $C_6H_9Na_3O_9$. After extraction, the supernatant was cleaned up using dispersive solid-phase extraction. A mixture of 36 pharmaceuticals was selected to spike the samples in order to properly evaluated the different working modes- Sensitive and selective liquid chromatography–mass spectrometry (LC–MS) analysis is a powerful and essential tool for contaminant identification in environmental studies. An MS^2 (or tandem, MS/MS) mass spectrum is acquired from the fragmentation of a precursor ion by information-dependent acquisition (IDA) and MS/MS^{ALL} mass spectrum acquired with SWATH (sequential window acquisition of all theoretical fragment-ion spectra). We compared these two techniques in their capabilities to produce comprehensive MS^2 data by assessing both contaminant MS^2 acquisition hit rate and the quality of MS^2 spectra, also the difference between use fix window SWATH (FSWATH) and variable window SWATH (VSWATH) were also studied. Both SWATH methods were able to identify a higher number of compounds in all the analyzed samples than IDA. However, FSWATH provides slightly better information than VSWATH. On the other hand, the useless spectral information (coming from background noise and interferent peaks) is higher using SWATH modes. This multiplies the time spent to process the data of the chromatogram. The method used is suitable to detect different emergent pollutants in biotic and abiotic matrices as river sediment and mussels showing interesting prospects within the field.

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P-EA-09

ANALYSIS OF PESTICIDE RESIDUES IN HONEYBEES, POLLEN AND BEESWAX BY QUECHERS EXTRACTION AND LC-MS/MS DETERMINATION

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Pesticides affect several non-target beneficial insect, such as honeybees, being not only able to kill them but also to contaminate beehive products. This study aimed at developing multiresidue methods for monitoring 62 pesticides and degradation products in honeybees, pollen and beeswax by liquid chromatography-tandem mass spectrometry (LC-MS/MS).

Pollen and honeybee samples (5 g) were extracted following a modified QuEChERS protocol using acetonitrile (10 mL) followed by a dispersive solid phase extraction clean up with PSA and C_{18} (50 mg) to remove sugars, fatty acids and nonpolar interferences [1, 2]. Beeswax samples were also extracted with acetonitrile by melting wax in a water bath at 80 ºC and then, the extract was cool (−18 °C, for at least 2 h) for precipitation of the wax. Finally, 25 mg PSA and 25 mg C18 were added for clean-up and pH was adjusted to 5 [3]. The resulted extracts were then analysed by LC-ESI-MS/MS in positive mode. Separation was carried out on a Luna C18 column (150 × 2.0 mm, 3 µm) using a gradient elution profile with mobile phase consisting of water-methanol both, 10 mM ammonium formate. The two most intense precursor ion → product ion transitions were monitored to obtain unambiguous confirmation of the compound identity.

The sensitivity of the methods was estimated by establishing the limits of detection (LODs) and quantification (LOQs). In pollen matrix LODs were lower than 2 $ng \cdot g^{-1}$ and LOQs were below 5 $ng \cdot g^{-1}$ for all pesticides. Honeybees matrix showed LODs from 0.3 to 3 $ng \cdot g^{-1}$ whereas LOQs ranged from 1 to 10 $ng \cdot g^{-1}$. In beeswax, LODs were from 0.3 to 4.2 $ng \cdot g^{-1}$, whereas LOQs ranged from 1 to 12.5 $ng \cdot g^{-1}$. Precision, expressed as relative standard deviation (RSD), was < 20% in most pesticides analyzed. Matrix effects were mostly suppressive in the three matrices and ranged from -60 to 50% over the response of the standards prepared in solvent. The average recoveries values were 89, 70 and 83% for pollen, honeybees and beeswax, respectively.

Wax and pollen were the most contaminated matrices and exhibited a wide contamination by pyrethroids and organophosphates. Acaricides used in beekeeping, such as coumaphos, chlorfenvinphos, amitraz and fluvalinate were the most frequently detected pesticides in wax. Neonicotinoid acetamiprid and organophosphates chlorpyrifos and dimethoate were detected in pollen samples. Honeybee samples were less contaminated, although some acaricides and insecticides were found in this matrix.

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P-EA-10

EFFECT OF CLIMATIC VARIABILITY IN THE SOIL ORGANIC MATTER COMPOSITION STUDIED BY ANALYTICAL PYROLYSIS

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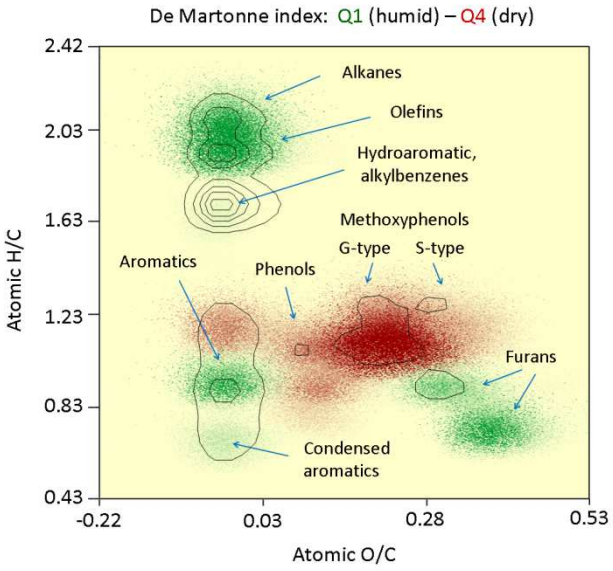
In present days there is a growing concern about the progress of desertification in different areas of the world. The unsuitable management of the soils and the change of land use may increase the desertification risk. On the other hand, desertification is typically associated with the decrease of soil organic matter (SOM) levels with the consequent loss of fertility in the soil. Presumably, all these aspects are reflected in the molecular composition of SOM. Previous studies have evidenced that a correlation exists between the carbon sequestration efficiency and the relative abundance of specific SOM constituents, e.g., alkane homologous series [1] or lignin-derived methoxyphenols [2]. This study aims to identify molecular descriptors of the SOM composition, which are responsive for the impact of climate, quantified with bioclimatic indices defining a continuous gradient between wet and dry areas. A total of 33 soil samples were collected from different areas of Spain. The studied soils presented a large variability in their chemical and physical properties, and were developed under different geological substrate and vegetation type. The sampling was carried out in the topsoil (0–10 cm) where the SOM content is higher.

In order to assess desertification levels we used the De Martonne aridity index. This index was calculated from the annual average rainfall and annual average temperature for each soil sampling point. The SOM was analyzed by pyrolysis - gas chromatography mass spectrometry (Py-GC/MS) of whole soil samples. A total of 193 pyrolysis compounds were identified, and used as predictor variables in Partial Least Squares (PLS) regression models forecasting the De Martonne aridity index. The results showed that a significant prediction of this index (R = 0.869) exclusively using the information provided by Py-GC/MS analysis of the corresponding soils is possible. A graphical-statistical method based in the classical van Krevelen diagram was used for displaying the pyrolysis results [3], representing difference values between the proportions of the 193 pyrolysis products, calculated between average pyrograms for soils in the uppermost quartile of the De Martonne index, and the average of those in the lower quartile. These values are shown as a scatterdiagram where the coordinates in the plane of the individual molecules correspond to their H/C and O/C atomic ratios, calculated from their empirical formulas. The difference values between relative abundances were represented as a density map where the green colour indicates



compounds predominant in the SOM of soils formed in sites with high De Martonne index, and the red colour indicate compounds predominant in soils with low index (i.e., comparatively dry ecosystems). The Student's *t* (p > 90%) was also used to evaluate the significant differences between the proportions of compounds, and was represented as a superimposed contour diagram in the Figure.

The progressive desertification of the soils is associated to a molecular composition of the SOM defined by the selective accumulation of lignin-derived compounds at different stages of transformation in soil (phenols and methoxyphenols), whereas aromatic compounds and aliphatic hydrocarbons tend to be major SOM constituents in soils developed under comparatively humid climatic conditions. As a whole, the results suggests that progressive evolution towards arid climate leads to a decrease in SOM quality, as reflected by the accumulation of raw organic matter where structural units of plant macromolecules can still be easily recognized. Conversely, in soils formed in ecosystems with comparatively longer wet season, the SOM formation is carried out at expenses of the incorporation of aliphatic material of plant and microbial origin (mainly alkenes and alkanes) together with condensed aromatic structures, which are traditionally considered as typical pyrolytic products from humic substances, with high resilience or resistance to biodegradation.

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P-EA-11

ANALYTICAL CHALLENGES OF ANALYSIS OF POLLUTANT INCLUDED IN "WATCH LISTS OF WATER FRAMEWORK DIRECTIVE" BY LC-MS/MS AND HRMS

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The Water Framework Directive (WFD) aims on maintaining and improving the aquatic environment in the Member States. One of the actions of developing WFD is to provide high-quality monitoring information on the concentrations of emerging pollutants. Based on this, Commission Implementing Decision 2015/495/EU [1] established the first Watch List of Substances, as defined in the article 8b of Directive 2008/105/EC [2], for water monitoring. During 2017, the Commission analyzed the data from the first watch list and based on that data, the Commission has modified this list for Union-wide monitoring in the field of water policy pursuant to Directive 2018/840/EC [3]. The substances belonging to the first and second Watch List susceptible to be analyzed by liquid chromatography-mass spectrometry (LC-MS) are the following: Neonicotinoid pesticides (Imidacloprid, Thiacloprid, Thiamethoxam, Clothianidin and Acetamiprid), Macrolide antibiotics (Erythromycin, Clarithromycin and Azithromycin), Diclofenac, Metaflumizone, Amoxicillin and Ciprofloxacin.

The routine study of several pollutants in environmental samples is usually based on using robust and quantitative LC-MS/MS approach by QqQ instruments for target analysis [4]; however, this strategy does not allow the screening of non-targeted metabolites or degraded products [5]. Additionally, another significant challenge in the analysis of organic pollutants by LC-MS/MS is the confirmation of each compound by monitoring two transitions and calculating their ratio of areas according to Decision 657/2002 [6]. In this respect, the second transition is often much less sensitive, for example in the case of Diclofenac (object of study) or even non-existent as it happens with Ibuprofen. Thus, the aim of this work is to carry out the analysis by liquid chromatography-high resolution mass spectrometry (LC-HRMS, Orbitrap), for screening analysis of metabolites and transformation products and for identification confirmation by accurate mass measurement and their characteristic isotopic profile.

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P-EA-12

DETERMINATION OF HIGH VOLUME PRODUCTION CHEMICALS IN OUTDOOR AIR PARTICULATE MATTER. ASSESSING THE HUMAN EXPOSURE.

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High volume production (HVP) chemicals have a widespread use in various applications and are present in several products used on a daily bases. Among them, benzothiazoles (BTHs), benzotriazoles (BTRs), benzenesulfonamides (BSAs), organophosphate esters (OPEs) and phthalate esters (PAEs) have become a great concern in the past decades. Several of these chemicals have shown to be harmful to human and have been subject for legal regulation in order to control the production and use of these chemicals [1, 2]. Because of their extensive use, these chemicals can easily reach environmental matrices, and their presence have already been reported in water, soil and air. Their presence in the atmosphere can occur due to volatilization from the original source and they can be partitioned among the two compartments, gas phase and particulate matter [1-4].

In this sense, a method based on gas chromatography-mass spectrometry (GC-MS) combined with pressurized liquid extraction (PLE) to simultaneous determine seven OPEs, six PAEs, four BTRs, five BTHs and four BSAs in the particulate matter samples from outdoor air has been developed. Under the optimal conditions, these contaminants can be extracted from the matrix with recoveries greater than 75%, for most of the compounds. The developed method enables the detection of these contaminants at levels of low pg m^{-3} with high repeatability (%RSD (n=3) values lower than 15%).

Several samples from an urban site influenced by the industries located in the vicinity and other samples from an industrial location were collected and analyzed under the optimal conditions. Therefore, the results obtained from the sampling points were a useful tool to be able to assess the human exposure via ambient inhalation of the population living near. Moreover, a human health risk was also characterized via inhalation as intake pathway.

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P-EA-13

APPLYING LC-HR-MS SUSPECT SCREENING FOR THE DETECTION OF PHOTOTRANSFORMATION PRODUCTS OF PHARMACEUTICALS IN SURFACE WATERS

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Industrial and municipal wastewater and manure are constantly entering in surface waters polluting directly its water quality. Thousands of wastewater-borne pollutants, including pharmaceuticals, have been detected in river samples but their concentrations along a river change constantly due to additional inputs on the one hand and losses due to natural attenuation processes on the other hand. Drugs can undergo phototransformation reactions by either direct or indirect photolysis including reactions giving rise to transformation products. To evaluate these processes in a river, usually laboratory studies are performed in a first stage and then, in the next step, studies are conducted directly in the natural environment. In our group, we have been following a workflow consistiting of the combination of high-resolution mass spectrometry (HRMS) acquisitions and processing software for evaluating the phototransformation of pharmaceuticals on a single compound basis under simulated and real environmental conditions.

Here we propose a new approach to evaluate the photodegradation of a cocktail of human drugs subject to transformation process. We first determined the presence of parent compounds (pharmaceuticals) along a river stretch in order to identify those with apparent attenuation. Next, we performed photolysis studies of the detected drugs under simulated solar light (Suntest apparatus) and characterized the phototransformation products by LC-HRMS. Finally, we reanalyzed the surface water samples for photoTPs to obtain evidence for in-stream photolysis. We detected 25 photoTPs of pharmaceuticals in the photolysis experiments, most of which originating from simple transformation reactions. Until now only one photoTP could be attributed to originate exclusively from phototransformation (Acetaminophen (AAP)-TP152) in the investigated river stretch. This provides evidence for photolysis as natural attenuation process in the river.

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P-EA-14

CATIONIC AMINE-BRIDGED PERIODIC MESOPOROUS ORGANOSILICA MATERIALS FOR OFF-LINE SOLID-PHASE EXTRACTION OF PHENOXY ACID HERBICIDES FROM WATER SAMPLES PRIOR TO THEIR SIMULTANEOUS ENANTIOMERIC DETERMINATION BY CAPILLARY ELECTROPHORESIS

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Phenoxyalkanoic acids are extensively used in agriculture. A filtering process may occur through the soils originating that these herbicides can achieve ground waters which can be polluted at concentrations in the µg/L levels. As a consequence, it is usually necessary to use a preconcentration process, such as solid-phase extraction (SPE), prior to their analysis.

In recent years, the application of mesostructured materials as new sorbents has considerably increased for sample preparation. In this work, two new mesoporous organosilica materials (PMOs) using styrylmethylbis(triethoxysilylpropyl) ammonium chloride (STPA) or bis(3-triethoxysilylpropyl)amine (TEPA) and tetraethylorthosilicate (TEOS) as silica sources were synthesized enabling ion-exchange or reversed-phase/ion-exchange mixed mechanisms, respectively, for the off-line SPE of a mixture of six phenoxy acid herbicides (fenoprop, mecoprop, dichlorprop, 4-CPPA, 3-CPPA, 2-PPA) from water samples previous to their analysis by CE. The use of a dual chiral selector system (20 mM TM-β-CD - 7 mM HP-β-CD) in 50 mM phosphate buffer at pH 7.0 enabled the simultaneous enantiomeric separation of the phenoxy acid herbicides in 11 min.

Although interesting characteristics with good recovery values for phenoxy acid herbicides from several water samples were shown by PMO-TEPA material, PMO-STPA was found to be the best sorbent for the off-line SPE of the compounds studied. Under the optimized conditions, it was demonstrated that using 100 mg of PMO-STPA sorbent, a maximum preconcentration factor of 1500 was achieved with 750 mL of solution, allowing recoveries between 75.5 and 112.2%. Analytical characteristics of the method were evaluated in terms of precision, linearity and accuracy with method quantitation limits between 0.4 and 14.3 µg/L. The method was applied to the analysis of river samples and effluents from wastewater treatment plants, with recoveries ranging from 78.3 to 107.5%.

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P-EA-15

SIMULTANEOUS ENANTIOMERIC DETERMINATION OF DRUGS IN WATER SAMPLES BY CAPILLARY ELECTROPHORESIS AFTER SOLID-PHASE EXTRACTION WITH PERIODIC MESOPOROUS ORGANOSILICA MATERIALS

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Periodic mesoporous organosilicas (PMOs) are organic-inorganic hybrid materials that combine the properties of the organic functionality (with ligands) and the chemical stability of the inorganic silica. In this work, a simple method of synthesis has been used for the preparation of three differents PMOs; two of them, with a neutral phenylene-bridged ligand, 1,4-bis(trimethoxysilylethyl)benzene (PMO-TMSEB-1 and PMO-TMSEB-2), from which one of them used tetraethyl orthosilicate as additional silica source (PMO-TMSEB-2). A third material was also synthesized with 1,4-bis(triethoxysilyl)benzene ligand (PMO-TESB-1). The three materials were evaluated as solid-phase extraction (SPE) sorbents for the off-line extraction of a mixture of seven drugs of different nature (duloxetine, terbutaline, econazole, propranolol, verapamil, metoprolol, and betaxolol) from water samples. Subsequent simultaneous enantiomeric analysis by CE, using sulfated-β-cyclodextrin (2% w/v) - 25 mM phosphate buffer (pH 3.0) and a voltage of -20 kV (negative polarity) was carried out. Enantiomeric resolutions ranging from 2.4 to 8.5 were obtained in an analysis time of 16 min. After optimization of SPE parameters, it was shown that using 100 mg of PMO-TESB-1 as sorbent, a preconcentration factor of 400 with 200 mL solution was achieved, allowing recoveries between 80.5 and 103.1% (except for terbutaline).

Analytical characteristics of the method were evaluated with method quantitation limits between 5.6 and 21.9 µg/L. The developed method was applied to the analysis of spiked wastewater samples collected in different treatment plants, with recoveries between 73.9 and 102.9% except for econazole for which recovery values ranged between 58.5 and 72.4%.

The results presented in this work show the potential of the use of PMOs materials as sorbents for off-line SPE previous to CE separation in the simultaneous chiral analysis of drugs from water samples.

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P-EA-16

ASSESSMENT OF POPs IN MARINE MAMMALS FROM THE MEDITERRANEAN SEA

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The Mediterranean Sea represents a marine biodiversity hot spot. At the same time, its coastline is one of the most densely populated in the world with high rates of industrialization, tourism and transportation routes. Anthropogenic pollution represents, in consequence, a heightened pressure that this world's largest semi-enclosed basin undertakes today [1]. Persistent organic pollutants (POPs) are of particular concern upon the risk of adverse effects they pose to public health and wildlife, derived from their toxicity, persistence in the environment, capability of long-range transportation and accumulation and biomagnification in food webs. The highest POP concentrations are frequently described in apex predators such as cetaceans, particularly odontocetes.

The aim of this study was to assess the degree of contamination by dl-PCBs, PCDD/Fs and PBDEs in two representative species of odontocetes in the Mediterranean Sea: the striped dolphin and the sperm whale. Samples of subcutaneous blubber were obtained from stranded specimens between 2008 and 2016 and were analyzed for dl-PCBs, PCDD/Fs and PBDEs using GC-HRMS. Quantification was carried out by the isotopic dilution technique.

All target POPs were detected in the two species investigated in this study. PCBs and PCDD/Fs were significantly higher in sperm whales than in striped dolphins. The relative abundance of target pollutants was the same in both cetacean species and followed the order dl-PCBs>PBDEs>>PCDD/Fs, which is in consonance with what has been reported in recent studies conducted on Mediterranean cetaceans [2]. Main contributors to TEQ values were dl-PCBs accounting for over 93 and 96% of total TEQs, in the case of striped dolphins and sperm whales, respectively. However, the contribution of each group of dl-PCBs varied depending on the species. TEQs for all sperm whale specimens and one striped dolphin surpassed the threshold of 210 pg WHO-TEQ/g l.w. in blubber, proposed as starting point of immunosuppression [3].

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P-EA-17

PRESENCE AND ELIMINATION OF CONTAMINANTS OF EMERGING CONCERN THROUGH A TREATMENT LINE FOR LANDFILL LEACHATE REMEDIATION

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Landfill leachate results from the percolation of water through solid waste. This type of wastewater presents low biodegradability and normally high acute toxicity. Leachates are usually discharged into the environment or end in municipal wastewater treatment plants (WWTPs), which are not effective in the treatment of biorecalcitrant landfill leachate.

Characterization of landfill leachates have been usually performed by determinig several global parameters (i.e. TOC, DOC, COD, BOD, total phenols, etc.). These parameters do not provide information about the organic pollution and potential environmental impact if reach groundwater or surface waters and thus efforts have been made for their characterization at molecular level. Compounds reported include among others a variety of aromatic hydrocarbons, phenols, chlorinated aliphatics, pesticides, or plastizers. However, knowledge on the presence of contaminants of emerging concern (CECs), although relevant, is still very limited.

In this work an analytical procedure based on direct injection liquid chromatography tandem mass spectrometry (DI-LC-MS/MS) has been applied to evaluate the presence and fate of 115 CECs throughout a treatment line proposed for landfill leachate remediation. The treatment line consists on a physicochemical pre-treatment; an advanced chemical oxidation step, based on solar photo-Fenton process, and an advanced biological treatment, based on immobilized biomass reactor (IBR). Results obtained reveals that, even when a high removal rate (>90%) is reached at the end of the treatment, the final effluent still contain relevant concentrations (>50 mgL-1, expressed as total charge of CECs), similar than those reported in municipal wastewaters, thus reinforcing the relevance of this pollution source.

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P-EA-18

DIFFERENT TYPES OF SOLID PHASE EXTRACTION FOR ABOUT 30 ORGANIC COMPOUNDS, SUCCESSIVELY DETERMINED BY HPLC/MS-MS (QqQ)

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In the last years, the interest in detecting environmental contaminants in different matrices (mostly sediment, soil and water) is increasing because their more relevant impact on the global ecosystem [1]. In this study, we focused on determination of Pharmaceutical Compounds and Personal Care Products. The study was conducted on about 30 compounds, including acid, basic and neutral. The selected compounds constitute an important block of organic contaminants frequently found for many reasons, such as industrial waste, expired or unused medicinal product not disposed in the right way, and excretion of drugs and their metabolites derived from therapeutic treatments [2]. Some of the selected compounds as metformine required a careful optimization of the extraction conditions. The analytical method was based on solvent extraction (if a solid matrix is used) followed by solid-phase extraction (SPE). The chromatographic separation was performed using an Agilent 1260 ultra-high performance liquid chromatography (UHPLC) with a Phenomenex Kinetex C_{18} column of 1.7 µm of particle size at constant flow rate of 0.2 mL min^{-1}. The mobile phase consisted of deionized water and methanol, both with 0.1% formic acid (for positive mode) and with 0.1% ammonium fluoride (for negative mode), working in gradient mode. The UHPLC was coupled to an Agilent 6410 triple quadrupole mass spectrometer with an electrospray ionization source working both in positive (ES+) and negative mode (ES-). Different steps of the extraction procedure were considered to optimize the recovery of the compounds. Regarding the solid-phase extraction (SPE), 2 different stationary phases of cartridges were tested: *Phenomenex Strata-X 33 µm Polymeric Reversed Phase 200 mg/6 mL* and *Phenomenex Strata-X-CW 33 µm Polymeric Weak Cation 200 mg/6 mL.* Moreover, the activation of cartridges was considered before the passage of sample with and without the use of a 2mM Sodium Dodecyl Sulfate (SDS) solution. In each test the extracts were reconstituted with 1 mL of 70:30 water/methanol like the chromathographic mobile phase. Sediment and water samples were analysed. The recovery' results obtained are very interesting, ranging from 30% to 120%. The use of SDS solution improves the recovery of a number of compounds (mostly of basic character). As well as Polymeric Cation stationary phase has given good results for some compounds.

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P-EA-19

Monitoring of cyanotoxins in water by ultra-high performance liquid chromatography following salting-out assisted liquid-liquid extraction

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Cyanobacteria is a phylum of photosynthetic bacteria with a global distribution. They form the basis of numerous aquatic and terrestrial food chains and are finding increasing application in biotechnology although they may present also a risk to human and animal health due to the production of potent toxins, the cyanotoxins. This type of contaminants can accumulate in the food chain or we can have direct contact with them through polluted waters where mass growth of cyanobacteria occurs. It is therefore a major goal to obtain some adequate strategies for their detection and quantification [1].

The main objective of this work is the development of a new, rapid and sensitive method of analysis for a group of cyanotoxins, eight microcystins (MCs) (MC-LR, MC-RR, MC-LA, MC-LF, MC-LW, MC-LY, MC-YR, MC-WR) and nodularin (NOD), using ultra high performance liquid chromatography (UHPLC) as separation method with diode array detector. Different variables that influence the separation and quantification were optimized. The stationary phase selected was a Zorbax Eclipse Plus RRHD C18 (50 × 2.1 mm, 1.8 µm). A gradient elution program based on water and acetonitrile containing 0.01% of formic acid at a flow rate of 0.4 mL/min was used with an injection volume of 20 µL. The separation time was ~ 7 min. For detection, absorbance was measured at 240 nm. Once the optimal conditions were established, the method was validated by calculating the linear range of concentration, sensitivity, linearity and detection (LD) and quantification (LQ) limits for all analytes. LD and LQ between 5.6 –17.1 (µg/L) and 18.8 –57.1 (µg/L) were obtained respectively.

A facile, effective, and rapid sample preparation based on salting-out assisted liquid-liquid extraction (SALLE) has been optimized to determine the selected cyantoxins in seafood stuff and environmental samples. To obtain satisfactory extraction efficiencies for the studied analytes, several parameters affecting the SALLE procedure were optimized, such as type and volume of the extraction solvent and nature and amount of salt. The optimum values were 4 mL of sample, 2 mL of acetronitrile as extraction solvent and 1. 6 g of $(NH_4)_2\ SO_4$. Characterization of the method in terms of performance characteristics and application to different matrices are currently being carried out.

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P-EA-20

EMERGING POLLUTANTS IN SOIL AND PLANTS OF SAUDI ARABIA: CONSEQUENCES OF THE USE OF TREATED WASTE WATER FOR IRRIGATION

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Emerging contaminants (ECs) have been detected in the soil environment where there is the potential for uptake into crops. Previous plant uptake studies under controlled field conditions were done at unrealistic exposure concentrations [1]. This study was aimed to assess the presence of emerging pollutants in soils and crops irrigated with treated wastewater in Saudi Arabia to evaluate the potential of plant uptake of these compounds under environmental conditions. The use of LC-MS/MS continues being the best tool for detecting emerging contaminants in environmental matrices, the combined use of hybrid high-resolution mass spectrometry (HRMS) and ultrahigh pressure liquid chromatography (UHPLC) has been proved as a good method to study these contaminants [2,3].

Then, to improve performances, a triple quadrupole time-of-flight mass spectrometer (QqTOF), the Triple-TOF® (ABSciex, Darmstadt, Germany) with resolving power up to 35, 000 FWHM at m/z 200 was used. Furthermore, the Triple-TOF® system combines the TOF with a high-performance quadrupole, which allows the possibility of precursor ion fragmentation providing high sensitivity and selectivity. In this 'suspect screening', compounds of interest are not previously selected but a database containing information of a high number of them is used to identify potential substances present in the sample. The MS/MS spectra of every compound is analysed to discriminate the compounds detected. The study included suspected screening analysis of water sample for irrigation taken in four different sites after the South Riyadh wastewater treatment plant. In addition, soil and crops growing in the surroundings were also analysed.

Numerous emerging contaminants were found in water, soil and crop samples. These were for instance phenols, antioxidants, and plasticizers of the phthalate-type. Also a fibrates compound (Gemfibrozil, CAS: 25812-30-0) was frequently found in all sample types and in high concentrations, Gemfibrozil is a drug used to lower lipid levels. This compound increases the activity of extrahepatic lipoprotein lipase, by activating Peroxisome that is involved in metabolism of carbohydrates and fats. To our best knowledge it has not been detected before in plant samples. The detection of this emerging pollutants provides global information about the possible risk for the environment in this area of Saudi Arabia and others with similar conditions that are using treated waste water for irrigation.

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P-EA-21

COMBINED GC-MS AND CHEMOMETRIC APPROACH FOR THE COMPREHENSIVE ANALYSIS OF ORGANIC COMPOUND SOURCES IN RURAL AND URBAN ATMOSPHERES

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Gas chromatography coupled to mass spectrometry (GC-MS) was used for the analysis of atmospheric particulate matter (PM) fractionated in six aerodynamic sizes, >7.2, 7.2-3, 3-1.5, 1.5-1, 1-0.5, <0.5 µm, and volatile organic compounds. The samples were collected at urban and rural sites during warm and cold seasons. Markers of photochemically synthesized organic compounds or combustion sources, either biomass burning or traffic emissions, were predominantly observed in the fraction <0.5 µm whereas the larger particles were composed of mixed sources from combustion processes, vegetation emissions, soil re-suspension, road dust, urban life-style activities and photochemically synthesized organic compounds.

Important seasonal differences were observed at the rural site. In the <0.5 µm fraction these were related to strong predominance of biomass burning in the cold period and photochemically transformed biogenic organic compounds in the warm period, e.g. pinene oxidation products. In the 7.2 > PM > 0.5 µm fractions the differences involved predominant soil-sourced compounds in the warm period and mixed combustion sources, photochemical products and vegetation emissions in the cold. The strong predominance of biomass burning residues at the rural site during the cold period involved atmospheric concentrations of polycyclic aromatic hydrocarbons that were three times higher than at the urban sites and benzo[a]pyrene concentrations above legal recommendations.

Multivariate Curve Resolution Alternating Least Squares showed that these organic aerosols essentially originated from six source components. Four of them reflected primary emissions related with either natural products, e.g. vegetation emissions and up whirled soil dust, or anthropogenic contributions, e.g. combustion products and compounds related with urban life-style activities, mainly vehicular exhausts and tobacco smoking. Two secondary organic aerosol components were identified. They accumulated in the smallest (<0.5 µm) or in the larger fractions (>0.5 µm) and involved strong or mild photochemical transformations of vegetation precursor molecules, respectively.

P-EA-22

MICROPLASTIC POLLUTION IN THE ATLANTIC OCEAN: IDENTIFICATION OF POLYMER TYPES AND ADDITIVE CONTENT USING ANALYTICAL PYROLYSIS (PY-GC/MS)

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Plastic gradually fragments into smaller pieces forming microscopic fractions of less than 5 mm commonly known as microplastics. These microplastics have become one of the most persistent pollutants of the sea and beaches, due to their small size, their ubiquity and global distribution [1].

An estimated 80% of microplastics pollution comes from land, while about 18% of these marine debris is attributed to the fishing industry [2]. Moreover, previous studies reported up to 44% of raw pellets and values above 100g/l of sand in the coastal zones of the Canary Islands. The Canary Islands constitutes an area of accumulation of microplastics, being found this type of pollution even in beaches infrequently visited [3].

Microplastics represents a major threat to the environment due to the following reasons [4]:

- Are typically hydrophobic with large surface areas and high adsorption capacity of POPs (Persistent Organic Pollutants) and PBTs (Persistent, Bioaccumulative and Toxic substances).
- As they adsorb POPs, microplastics can result in a double-entry pollution vector: as a POPs vector and by the plastic itself.
- High abundance and long residence time.
- Absorption and ingestion by aquatic organisms and subsequent transfer to higher trophic levels.

Given that microplastic is a relatively new environmental problem and their newly increased pollution levels, it is important to better understand their impact. The establishment of standardized analysis procedures for their chemical characterization is required among the scientific community.

A total of 10 microplastic samples collected in the Canary Islands were optically characterized and analysed using pyrolysis-gas chromatography coupled to mass spectrometry (Py-GC/MS). The pyrolysis temperature was 400 ºC for 1 minute and the chromatographic conditions and compound assignment procedure are described elsewhere in [5]. The studied microplastics were mainly light polyolefins (polyethylene, PE and polypropylene, PP) but one that was found to be composed mainly of cellulose. Other compounds and additives associated with the microplastics, such as fatty acids, ketones and plasticizers (phthalates) were found with discriminant value to differentiate different polymers.

Py-GC/MS was found an appropriate tool for microplastic research. In this work it was possible to identify the nature of all samples studied, elucidate they polymer composition if any and also provide valuable information about origin and production line.

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P-EA-23

ANALYTICAL PYROLYSIS OF SOIL EASILY-EXTRACTABLE GLOMALIN (EEG) FRACTION

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Easily Extractable Glomalin (EEG) represents an organic fraction of the soil that contains mainly glomalin-related soil proteins (GRSP), a glycoprotein abundantly found in soils produced by arbuscular mycorrhizal fungi in the phylum Glomeromycota [1]. The EEG fraction is confirmed to have multiple ecological functions in soils, including the improvement of soil stability and resilience to degradation, facilitate aggregate formation and contribute to soil carbon storage [2]. Given its potential for soil C immobilization, a detailed molecular characterization "fingerprint" of pyrolysis products of EEG fraction extracted from a Mediterranean soil under different plant covers, affected and unaffected by forest fire and at different times is conducted.

A total of 16 samples were extracted from soils in Gorga (NE Alicante, Spain). Further information about the sampling process and EEG extraction protocols are described elsewhere [3]. In short, samples were taken from the surface (to 2.5 cm depth; A horizon) under pine and shrub covers, immediately after a forest fire (July 2011), and at 4, 8 and 12 months after the fire. Surrounding soils with similar characteristics but unaffected by fire were taken as control. The EEG samples were analysed using pyrolysis-gas chromatography coupled to mass spectrometry (Py-GC/MS). Pyrolysis temperature was 400 ºC for 1 minute and detailed chromatographic conditions and compound assignment procedure were as described in [4].

A total of 139 compounds were identified and grouped according to their probable biogenic origin: polysaccharides (PS), lignin and polyphenols (LIG), proteins and polypeptides (PRO), non-specific aromatic compounds (ARO), hydro-aromatics (HAR), lipids (LIP), polycyclic aromatic hydrocarbons (PAH) and terpenes (TER).

A remarkable high similarity was found between EEG samples from different plant covers, both affected and unaffected by forest fire and at different time over a year after the fire. This fact indicates that EEG is a structurally stable soil organic fraction, very homogeneous and highly resistant if temperatures remain below 200-250ºC [5]. Its chemical structure mainly accounted for PS (42 ± 5%), ARO (24 ± 3%) and HAR (12 ± 3%). The remaining 20% included PAH (8 %), LIP (7 %), LIG (5 %) and PR (2 %). Comparison with previous results prove EEG to be rich in aromatic carbon [6, 7] and this reinforces the idea of EEG having a role in carbon sequestration.

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P-EA-24

ANALYSIS OF POLYSTYRENE MICROPLASTICS BY LC-QEXACTIVE ORBITRAP IN COASTAL AREAS OF CATALONIA

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The enormous quantity of plastics in coastal waters, estuaries and oceans waters is a severe environmental problem. Consequently, under environmental conditions, plastic items are able to generate smaller fragments until nano- and microscopic sizes (known as nanoplastics (NPLs) and microplastics (MPLs), respectively)[1]. Accordingly, to the type of plastic, the density of these particles are variable and this may influence the bioavailability in the water column; thus, the presence of these contaminants in sediments as well as the polymers ingested by marine organism may vary [2]. In addition, rivers could transport MPLs to the downstream of the lakes and coastal environment, where they can interact with biota and the water ecosystem[3].

The main objectives of this work is to apply a validated method of liquid chromatography coupled to high resolution mass spectrometry (LC-HRMS) to determine the presence of polystyrene, one of the most frequent plastics used in the industry. The application of the methodology aims to assess the presence of selected compound in water samples from Mediterranean estuarine coastal area (Ebro Delta from Catalonia, Spain).

Due to the nature of MPLs/NPLs, advanced polymer chromatography (APC) coupled to APPI-HRMS-QExactive can be used for characterization of monomer types but also for a quantitative approximation due to the mass spectrometer employed. The sensitivity of the developed method presents a limit of detection (LOD) lower than 1 µg/L and allows to obtain qualitative and semi-quantitative information about high-molecular weight polymers, which may also be present in the environment.

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P-EA-25

SUBCRITICAL WATER COMBINED WITH MEMBRANE ASSISTED EXTRACTION FOR ATMOSPHERIC PARTICLE-BOUND PAHs DETERMINATION

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Typical techniques for extraction of particulate bound-PAH (shaking, Soxhlet, sonication, microwave-assisted or pressurized liquid extraction) use toxic solvents, frequently requires of clean up and concentration steps [1]. In this work, a green analytical methodology for the determination of 16 priority Polycyclic Aromatic Hydrocarbons (PAHs) and 8 related compounds in air particulate matter was developed and validated. The method was based on pressurized hot water extraction (PHWE) followed by miniaturized membrane assisted solvent extraction (MASE) and programmed temperature vaporization-gas chromatography–ion trap tandem mass spectrometry detection (PTV-GC-MS/MS). The extraction conditions were optimized by a Box-Beckhen design and desirability function evaluation [2].

In the optimized procedure six aliquots of the sampled filter were introduced in the ASE cell, and the surrogate labelled standards were added. The cell was extracted at 200ºC during 5 min of static time, using water as extractant with a 25% of MeOH as modifier. The PHWE extracts were brought to 40 ml with the water: MeOH (75:25) solution and 15 mL aliquot was MASE extracted by 90 min at 30ºC with a PP membrane insert containing 500 µL of internal standard solution. The extract was injected in the PTV-GC-MS/MS.

Relative recoveries obtained with the proposed method were between 78 and 118% and precision <22%. Quantitation limits of the method ranged from 0.9 to 75.6 pg. m^{-3}. SRM1649b reference material was analyzed with satisfactory results.

The optimized method agrees with the green analytical chemistry principles [3] and supposes an appropriate alternative to the most conventional methodologies of analysis of PAHs in air particulate.

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P-EA-26

COMPARATIVE RESPONSE TO TAMIFLU® (OSELTAMIVIR PHOSPHATE) UNDER WATER-EXPOSURE IN MUSSELS AND CLAMS

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Tamiflu® is the commercial brand name for the antiviral agent oseltamivir ethylester (OST). This compound can be found in the environment at low levels and toxic consequences of its exposure have been predicted to be low, except during pandemic events [1]. The aim of the present study was to assess a suite of biomarker responses, accumulation and metabolism associated to a sub-lethal water exposure to OST in two bivalve species (mussels and clams). The role of carboxylesterase (CE) in the biotransformation of this drug was studied. Potential harmful effects assessed by the activity of antioxidant enzymes and lipid peroxidation (LPO) levels were also addressed.

The bivalves were exposed to OST (100 µg/L) for 48h. The presence of OST and its derivate oseltamivir carboxylate (OST-C) was determined by liquid chromatography-mass spectrometry (LC-MS) in haemolymph, as well as activity of CE (with four substrates) and of the antioxidant enzymes glutathione reductase (GR), glutathione peroxidase (GPX), catalase (CAT) and glutathione S-transferase (GST), and LPO levels were determined in gills and digestive glands. Differences between control and treated individuals in terms of chemical and biochemical determinations were tested.

As regards analytical determinations, the new quadrupole time-of-flight MS system SCIEX X500R QTOF was used to identify OST and its metabolite. Neither OST nor OST-C were detected in the control groups. Both were detected in treated mussels, and only OST in treated clams, and at lower levels than in mussels, indicating higher uptake and metabolism of OST in the latter bivalve. Regarding biochemical determinations, significant differences in CE activity (substrates 1-NA and 1-NB in mussels, substrates pNPA, pNPB, 1-NA and 1-NB in clams) between control and treated groups were observed in the digestive gland of the two bivalve species, pointing to enhanced biotransformation processes due to OST exposure and a tissue-specific response. As for oxidative-stress related biomarkers, significantly higher GR activity in mussel gills, higher LPO levels in clam gills and higher GST and CAT activities in clam digestive gland in the treated group could indicate induction of oxidative stress by OST exposure, manly in clam, although these results in antioxidant defenses remain inconclusive.

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P-EA-27

MULTIRESIDUE ANALYSIS OF PERSONAL CARE PRODUCTS IN CONTINENTAL WATERS BY SOLID-PHASE MICROEXTRACTION-GAS CHROMATOGRAPHY TRIPLE QUADRUPOLE MASS SPECTROMETRY

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The determination of personal care products in environmental samples is an important subject in water quality control. They are a multiclass family of emerging pollutants continuously introduce in environment waters though domestic, industrial discharges, and water recreational activities such is the case of the UV filters. Their presence may constitute and hazard for the health and the environment. In fact, they are starting to be included in environmental monitoring programs. The lack of suitable analytical methodologies makes necessary to develop multiresidue methods that include a high number of target compounds of different families in one analysis.

A method based on solid-phase microextraction-gas chromatography tandem mass spectrometry (SPME-GC-MS/MS) is proposed to determine more than 40 compounds including allergenic fragrances, musks, plasticizers, preservatives, and UV filters in environmental waters. SPME provides a high concentration factor and its combination with GC-MS/MS analysis working in SRM mode, provides high sensitivity that is essential to analyses these samples, where the compounds are found at levels of ng L^{-1}. The method was developed and optimized, and a multifactorial ANOVA was carried out. The selected conditions comprise the head-space extraction mode, with the polyacrylate fibre at 100ºC, and the addition of 20% (w/v) of NaCl. The chromatographic analysis was finished in 22 min and the extraction time was set at 20 min to achieve high throughput. Full validation of the method was performed. Linearity was studied in a broad concentration range from 0.1 to 1000 ng L^{-1} and satisfactory R^2>0.9925 were obtained in most cases. Recovery studies were performed at three concentration levels in real samples, and were in general between 85-110%. The method was applied to a high number of river water samples collected in the summer season and 30 of the analytes were found in the samples at concentrations between 0.044-610 ng L^{-1}, demonstrated the presence of these compounds in the environment.

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P-EA-28

DETERMINATION OF NEONICOTINOID INSECTICIDE RESIDUES IN WATER SAMPLES BY MICELLAR ELECTROKINETIC CAPILLARY CHROMATOGRAPHY

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Neonicotinoids (NNIs) are a class of insecticides widely used since the early 1990s for pest control. Their effectiveness using low amounts and their long permanency make them especially suitable for extensive farming. Due to their high polarity and solubility in water, they are taken up by the plant and transported throughout leaves, flowers, roots and stems, being found also in pollen and nectar. In foodstuffs of plant origin, it is crucial to ensure that they do not exceed the maximum residue limits (MRLs) regulated by the Europe Union (EU) [1]. Moreover, they have being related with the "Colony Collapse Disorder" syndrome, which involves the rapid loss of adult worker bees. For that, EU Commission restricted the use of plant protection products and treated seeds containing some NNIs (clothianidin, imidacloprid and thiamethoxam) [2]. For all these reasons, there is a need to evaluate the environmental impact and agricultural effects produced by neonicotinoids in different matrixes, such as bees and derived products, vegetables, fruits and environmental waters. Liquid chromatography coupled with UV detection and mass spectrometry has usually been the technique of choice.

In this work, micellar electrokinetic capillary chromatography (MEKC) is proposed for the simultaneous determination of seven NNIs (imidacloprid, acetamiprid, clothianidin, thiacloprid, thiamethoxam, dinotefuran and nitenpyram) and the metabolite 6-chloronicotinic acid. Separation was performed in a bare fused-silica capillary (48.5 cm x 50 µm, 40 cm effective length) using a background electrolyte consisted of 25 mM sodium tetraborate buffer (pH 9.2), 120 mM sodium dodecyl sulfate (SDS) and MeOH (15% (v/v)). Separation takes place at 25 °C and the applied voltage was 27 kV. Aqueous samples were hydrodynamically injected applying 50 mbar for 12s. To increase sensitivity, off-line preconcentration was achieved by solid-phase extraction using OASIS HLB cartridges. The proposed method showed satisfactory performance characteristics for its application in different kind of environmental waters.

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P-EA-29

STRUCTURE OF BIOCHARS PRODUCED FROM HYDROTHERMAL CARBONIZATION AND PYROLYSIS OF ORGANIC WASTE AND THEIR POTENTIAL USE AS N FERTILIZERS

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There is an urgent necessity of a sustainable management for the increasing quantity of organic waste such as sewage sludge (SS) or agricultural residues. Biochar (BC) is the carbonaceous solid residue produced through the thermochemical conversion (pyrolysis) of biomass under low O_2 atmosphere [1]. BC can act as a soil conditioner by retaining nutrients and improving soil physical and biological properties. Furthermore, the use of BC for managing urban wastes and generating added value products is gradually being more recognized. Nevertheless, char properties are highly dependent upon feedstock and pyrolysis process. Thus, if the mechanisms involved in the transformation of biomass into BCs are known it would be possible to infer the process to functionalize the product according to the intended final use. This hypothesis has remarkable implications for the potential use of BCs as N-fertilizer and soil conditioner. De la Rosa and Knicker [2] demonstrated that a significant part of the organic nitrogen contained in pyrogenic organic matter (OM) from plant residues was bioavailable. A comparable behavior for chars produced from other N-rich sources like SS is expected. This study attempts i) understanding the reactions/mechanisms involved in the formation of BCs from organic waste, and ii) assessing the applicability of chars as N-rich soil ameliorants. Thus, biochar from SS and rice husks (RH) were produced by applying dry pyrolysis (PY-600 ºC; 20 min) and hydrothermal carbonization (HTC; 200 ºC, 30 min; p=10 psi). In addition, ^{13}C and ^{15}N-enriched SS was used to produce HTC and PY ^{13}C and ^{15}N labeled BCs (samples ^{13}C-^{15}N-SS-Py600 and ^{13}C-^{15}N-SS-HTC200). Total C and N content decreased during pyrolysis of SS, whereas maintained almost constant for RH. H/C_{at} ratios decreased (<0.7) significantly for Py-chars pointing to a significant increase of the condensation degree. The isotopic signature of light elements ($\delta^{13}C$ and $\delta^{15}N$) determined different turnovers and dynamics of biomass transformation during the pyrolysis process for HTC and PY processes. Analytical pyrolysis (Py-GC/MS) was able to discern OM transformations that occurred during the pyrolysis process (dry and hydrothermal) at a molecular level. The pyrogram obtained for SS-HTC200 was similar than the original feedstock (SS). It was dominated by N-containing heterocycles, fatty acids and sterols. Dry PY at 600ºC removed the cholestanes but increased the abundance of polycyclic aromatic hydrocarbons. Finally, pyrolysis $\delta^{13}C$ compound specific isotopic analysis (Py-CSIA) was used to monitor the dynamics of organic compounds during the pyrolysis process and to discern the origin of the newly formed structures.

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P-EA-30

ANALYSIS OF POLYESTIRENE BASED MICROPLASTICS IN ENVIRONMENTAL SAMPLES

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Marine anthropogenic litter is a severe environmental problem [1]. One of the main issues is the extreme stability of plastic wastes. Under environmental conditions, the erosion of these materials generates smaller fragments some of them in the nano- and microscopic scale, which are known as nanoplastics (NPLs) and microplastics (MPLs), respectively [2]. The quantitative analysis of these plastic particles is particularly difficult and different approaches should be considered. In this context, this study was focused on the investigation and practical comparison and combination of different analytical tools for the quantitative and qualitative analysis of MPLs/NPLs using: (1) techniques to assess the physicochemical properties such as Thermogravimetric Analysis or TGA, Differential Scanning Calorimetry or DSC, and Fourier-Transformed Infrared Spectroscopy or FT-IR); (2) quantitative information by HPLC-MS. These studies have been carried out using as a representative polymer the polystyrene (PS), which is one of the most frequently used for plastics production.

The use of TGA, DSC and FT-IR was shown to be a useful tool for the characterisation and identification of polymers. However, it should be noted that they cannot be used as accurate quantification techniques. Using mass spectrometric analysis, the ionisation sources (ESI, APCI, APPI and MALDI) were optimized in negative/positive mode and their optimal parameters will be thoroughly discussed. The chromatographic separation was achieved by size-exclusion with a gel permeation column (GPC, Phenogel 5µm 50Å, Phenomenex) and using toluene 100% as mobile phase flowing at 0.5 ml/min. Finally, mass spectrometric analyses were carried out using a Q Exactive mass spectrometer, acquiring in full-scan mode with a resolution of 17,500 full widths half maximum (FWHM measured at m/z=200).

The best results were obtained by HPLC-HRMS equipped with atmospheric pressure photoionization (APPI) source operating in negative mode. The ionisation of PS resulted in a characteristic profile of signals, each of them centred at $[(C8H8)nH]\cdot^{-}$, and separated by 104 m/z. The APPI source was by far the most efficient ionisation. The environmental analysis of polymers should rely on a protocol, which combines different types of techniques for the complete characterisation of the whole spectrum of polymers that may occur.

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P-SP-01

DETERMINATION OF PHENOLIC COMPOUNDS IN TEA BY USING CYCLODEXTRIN-METHACRYLATE HYBRID MONOLITHIC MATERIALS

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Tea, a resource of our environment that is used by millions of people, is man's most widely consumed beverage except water. It is considered a rich source of polyphenols, which are known to act as antioxidants. However, there have been found traces of other phenolic derivatives in it that could not have such positive effects in health. A good example is the founding of phenol and all isomers of cresol in black tea [1], which are classified as volatile organic compounds and present, in fact, certain toxicity.

In this work, the efficiency of new materials made from modified β-cyclodextrin bounded to a polymeric network is evaluated through the development of an analytical method that combines solid-phase extraction with gas chromatography coupled with mass spectrometry detection to determine phenolic compounds in tea samples. Specifically, cyclodextrin has been used in this case as a surface ligand to a porous methacrylate-based monolithic material (GMA-co-EDMA). This phase has been studied as an alternative to the previously developed silica-cyclodextrin materials [2,3] that were applied to water preconcentration and air sampling in the past.

The developed method has good repeatability, with coefficients of variation of between 1% and 7%. Moreover, quantification limits were of approximately 5 μg L^{-1} for all analytes except for vinylphenol, whose sensitivity is lower. Recovery values were of around 90% in all cases except for phenol and guaiacol, and the method was compared with a reference method for phenolic compounds determination through solid-phase extraction. Due to the obtained results, this material may represent an alternative for phenols analysis in tea samples.

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P-SP-02

SYNTHESIS OF GROUND POLYMERIC SORBENTS WITH CYCLODEXTRIN NANOPARTICLES FOR ANALYTICAL APPLICATIONS

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Cyclodextrins have been identified as promising nanoscale carriers. Their property of being modified by their external hydroxyl groups has conducted to the possibility of immobilizing them by bonding or by inclusion in different supports, such as the organic ones. This has given the chance of designing new types of materials, which has given rise to a certain resurgence of cyclodextrins in Analytical Chemistry.

In this way, porous polymeric monoliths have been developed interestingly during the last decades, when they have become popular not only as stationary phases but also in other applications. Thereby, glycidyl methacrylate (GMA), which has an epoxy group at its structure, has been used as monomer to obtain functionalizable monoliths. The most common way of functionalizing them is by incorporating thiol groups on their surface, which can react either via radical or catalyzed processes under soft conditions with different types of substrates, such as cyclodextrins. This makes them suitable as reactive agents on polymeric materials for their surface modification through click-chemistry reactions.

However, to date, there have been reported few works focused on the synthesis of this type of materials for sample treatment in the analytical field. Some examples are those GMA-based materials in powder that have been showed to be helpful as an entrapment support to immobilize biomolecules [1], an also GMA-based monoliths that have been used for holding silver and gold nanostructures in them with different applications [2].

In this work, polymeric materials have been studied as supports for cyclodextrin nanoparticles to synthesize ground monoliths that can have analytical applications.

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P-SP-03

AUTHOMATED DETERMINATION OF INSECTICIDE METABOLITES IN URINE SAMPLES BY TURBOFLOW-LIQUID CROMATOGRAPHY COUPLED TO ORBITRAP MASS SPECTROMETRY

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Organophosphates (OPs) and pyrethroids are the most commonly used insecticides. These are non-persistent compounds and have become an alternative to persistent pesticides, such as organochlorines. [1]. However, human exposure to these compounds has been associated with several human health effects such as detrimental child neurodevelopment, decreased gestational age, altered serum hormone concentrations, wheeze and lung cancer [2]. Urine is the most frequently matrix used to biomonitor the concentration of OP and pyrethroid metabolites in humans [3]. The use of automated techniques for sample preparation, such as turbulent flow chromatography (TFC) or solid phase extraction (SPE), can be considered in order to increase sample throughput and to reduce the overall analysis time compared to traditional off-line methods.

In this study, liquid chromatography (LC) coupled to triple quadrupole mass spectrometry and LC coupled to high resolution mass spectrometry (HRMS) have been compared for the determination of six OP metabolites and three pyrethroid metabolites in urine samples. Despite triple quadrupole mass spectrometry provides better sensitivity, the Exactive-Orbitrap mass analyzer offers multiple advantages because its ability to analyze an unlimited number of compounds by means of accurate mass measurements combined with high resolving power, allowing selective detection of residues at low concentration levels in complex samples, such as urine. In the present work, off-line and on-line SPE and TFC have been compared for the analysis of insecticide metabolites in urine samples. Better results were obtained when on-line TFC were applied, which consists of a sample preparation system based on a column with large and porous stationary particles combined with a high flow rate of mobile phase. Taking into account the extraction and clean-up steps, the total analysis time was 13.83 min. For validation purposes, several validation parameters were determined such as recovery (83-116 %), repeatability (1-7 %) and reproducibility (2-19 %). Finally, the developed method has been applied in several urine samples, being the 4-nitrophenol the most detected compound at trace levels. Moreover, a retrospective screening analysis of a database of 1500 contaminants was carried out in the samples.

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P-SP-04

EXTRACTION AND DETERMINATION OF AFLATOXINS IN FOOD SAMPLES BY USING A NOVEL MESOPORUS SILICA-BASED SORBENT

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Mycotoxins are metabolites produced by fungi contaminating various food and feed crops, being a risk for both human and animal health. Mycotoxin contamination is an ongoing global concern and is considered an unavoidable and unpredictable problem, even where good agricultural, storage and processing practices are implemented. Thus, due to their carcinogenic and genotoxic properties, several health organizations recommend their control and vigilance especially in milk, fresh fruits and nuts [1,2].

In this work, the efficiency of silica-based mesoporous solid phases, belonging to the UVM-7 materials family [3], has been evaluated in the sample purification step, in order to preconcentrate several mycotoxins, specifically aflatoxins, by solid-phase extraction (SPE). The later determination of analytes has been carried out by high performance liquid chromatography with fluorescence detection.

For this purpose, synthesized material has been first characterized by several techniques such as Scanning and Transmission Electron Microscopy (SEM, TEM), X-Ray diffraction or N_2 adsorption-desorption. Then, several parameters that affected recovery through retention and extraction conditions have been optimized. Thereby, a new method for the determination of aflatoxins in food samples has been developed, and experimental results indicate that the UVM-7 material is an alternative for the most commonly used solid phases. Thus, quantitative recoveries have been achieved for all analytes (higher than 90 %) as well as good repeatability.

In addition, the method has been applied to aflatoxin determination in several food real samples, and matrix effect has been studied.

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P-SP-05

MOLECULARLY-IMPRINTED POLYMER-STIR CAKE SORPTIVE EXTRACTION OF ECGONINE METHYL ESTER FROM WATER AND BIOLOGICAL SAMPLES FOR THE EVALUATION OF COCAINE ABUSE

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Wastewater analysis is a rapidly developing scientific discipline with the potential for monitoring real-time data on geographical and temporal trends in illicit drug use. The method has been used to estimate illicit drug consumption in different European cities and in music festivals. Cocaine is the most popular abuse drug in Europe after cannabis, and it has been determined for the estimation of illicit drug use. The major cocaine metabolites excreted in urine are benzoylecgonine and ecgonine methyl ester, representing 30% and 18% of the administered doses, respectively [1].

In summary, the aim of this study is the development of a molecularly-imprinted polymer (MIP) for the ecgonine methyl ester extraction from wastewater and urine for the estimation of cocaine abuse. The main advantage of specific solid sorbents is that based on the reduction of the interfering compounds co-extraction which increases the mean lifetime of chromatographic columns, and decreases the limits of detection. Additionally, the stir cake sorptive extraction (SCSE) mode integrates extraction, enrichment and clean-up into one step, being its main advantages related to simple operation, high cost-efficiency, and high extraction capacity [2].

Extraction conditions such as sample pH, loading and elution time and elution volume were evaluated. Using the most appropriate extraction conditions, MIP-SCSE has been evaluated in terms of imprinting factor and loading capacity, obtaining values of 25 and 17.7 ± 0.3 µg per g of polymer, respectively. MIP-SCSE extracts have been analyzed by means of ion mobility spectrometry (IMS) as fast screening methodology and a liquid chromatography-mass spectrometry (UHPLC-MS-MS) reference procedure. Both methodologies have been validated in terms of linearity, trueness and precision. Quantitative recoveries were obtained for the analysis of spiked water and urine samples at concentration levels from 20 to 200 µg L^{-1}. Field water and urine samples were analyzed by both procedures obtaining comparable results with concentrations ranging from 0.025 to 0.25 ng mL^{-1} in water samples and from 0.03 to 50 ng mL^{-1} in urine.

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P-SP-06

ION MOBILITY SPECTROMETRY DETERMINATION OF DICHLOROPANE IN ORAL FLUID BY MICROEXTRACTION BY PACKED SORBENT

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New psychoactive substances (NPS) are defined by the United Nations Office on Drugs and Crime (UNODC) as substances of abuse which have similar effects to drugs under international control conventions, but not controlled yet. The NPS market is very dynamic and NPS belonging to diverse chemical groups are continuously emerging at an unprecedented rate. Dichloropane, also known as RTI-111, is a synthetic stimulant substance of the tropane chemical class, structurally related to cocaine with stimulant and anorectic properties and unknown pharmacology, metabolism, and toxicity in humans. Abuse drug consumption analysis is carried out in plasma and serum. However, the use of oral fluid as alternative matrix due to its simplicity and non-invasive collection is gradually increasing. Moreover, non-metabolized drugs are typically found in oral fluid analysis.

The usefulness of ion mobility spectrometry (IMS) for the analysis of NPS in biological fluids has been previously demonstrated after different sample treatments, such as liquid-liquid microextraction [1] and solid phase microextraction [2]. Microextraction by packed sorbent (MEPS) was introduced in 2004 as a simple, fast, on-line sample-preparation technique, with advantages like low sample and solvent consumption and high possibilities for automation [3]. Two different MEPS sorbents like octyl silica (C_8) and octadecyl (C_{18}) silica were evaluated for the extraction of dichloropane from oral fluids and its analysis by IMS, using a gas chromatography-mass spectrometry (GC-MS) procedure as reference method. Extraction conditions such as type of sorbent, sample pH, number of sample loadings, and elution volume were evaluated. The most appropriate conditions were selected for the analysis of synthetic saliva spiked with dichloropane at different concentration levels between 250 and 700 µg L^{-1}. C_{18} and C_8 solid sorbents provided quantitative results. The proposed procedure using C_{18} and C_8 MEPS has been validated in terms of linearity, trueness and precision. Blind spiked oral fluids collected from healthy individuals were analyzed by IMS and by a GC-MS reference procedure, being the results obtained from both methods statistically comparable.

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P-SP-07

MOLECULARLY-IMPRINTED PIPETTE-TIP EXTRACTION OF AMPHETAMINE-TYPE SUBSTANCES FROM ORAL FLUIDS

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Molecularly imprinted polymers (MIPs) are sorbents in which selected functional monomers are self-assembled around a template molecule, and then, polymerized in the presence of a cross-linker. After removing the template molecule from the MIP, a cavity complementary in shape and chemical properties is generated in the polymer structure, and becomes available to bind specifically template molecules. The main advantage of specific solid sorbents is that based on the reduction of the interfering compounds co-extraction which increases the mean lifetime of chromatographic columns, and decreases limits of detection. Those advantages are reflected in the number of applications of MIP extraction in a high variety of formats such as solid phase extraction (SPE) in cartridges, disks, capillary columns, dispersive SPE, magnetic SPE, solid phase microextraction (SPME), stir bar sorptive extraction (SBSE) and pipette-tips, among others [1].

In this study, the development of a molecularly-imprinted pipette-tip for the amphetamine-type extraction from oral fluids has been proposed. Polymerization conditions, monomer, cross-linker and porogen have been carefully studied and selected to provide appropriate permeability, absolutely necessary for pipette-tip SPE. In this approach, MIP was covalently linked to the pipette-tip during the polymerization reaction, thus, the use of cotton, glass wool or frites was not necessary. The MIP sorbent has been characterized using scanning electron microscopy and compared with the non-imprinted material (NIP). Extraction parameters such as sample pH, loading, washing and elution conditions were evaluated, using α-pyrrolidinopentiophenone, also known as α-pyrrolidinovalerophenone or α-PVP, a synthetic stimulant of the cathinone class, as target molecule.

Pipette-tip extracts have been analyzed by means of ion mobility spectrometry (IMS), as fast screening methodology, and a liquid chromatography-mass spectrometry (UHPLC-MS-MS) reference procedure. Both methodologies have been validated in terms of linearity, trueness and precision. Quantitative recoveries were obtained for the analysis of α-PVP in oral fluid samples at concentration levels from 50 to 250 μg L^{-1}. Reproducibility of the molecularly-imprinted pipette-tip has been also evaluated using 8 different units for the extraction of α-PVP in oral fluid at 250 μg L^{-1}, obtaining a relative standard deviation of 4 %.

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P-SP-08

EVALUATION OF GREEN ASPECTS OF ANALYTICAL TECHNOLOGY BASED ON DEEP EUTECTIC SOLVENTS FOR EXTRACTION OF BIOACTIVE COMPOUNDS FROM OLIVE LEAF

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Concerned about rising environmental impact and waste generated by the chemical industry, new strategies and analytical procedures have been proposed or revised with the aim to enhance a sustainable development [1]. Indeed, green analytical chemistry (GAC) emerged form green chemistry with the challenge of improving environmental friendliness of analytical methods.

Consequently, developing new green solvents is one of the key subjects in GAC in order to achieve a more eco-friendly media, shorter extraction times, simplicity, low cost and good extraction properties. In this sense, DESs seem to be promising green extraction solvents [2].

The green aspects of the methodology proposed based on DESs for the extraction of bioactive compounds from olive leaf have been evaluated in comparison with other analytical methodologies used with the same aim. For this purpose, an eco-scale based on assigning penalty points to parameters of an analytical process that are not in agreement with the ideal green analysis.

The analytical methodology based on deep eutectic solvents exhibited the highest eco-scale score due to the replacement of organic solvents by non-toxic ones. Furthermore, the use of this eco-friendly media meets with several principles of green analytical chemistry such as minimal amount of reagents, lower waste generation and safer solvents due to their low flammability and negligible vapor pressure [3].

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P-SP-09

COMPARATIVE STUDY OF THREE EXTRACTION PROTOCOLS FOR *VISCUM ALBUM L.* PROTEINS

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Mistletoe (*Viscum album L.*) has been recently investigated due to their supposed role in preventing some types of cancer. However, even if the knowledge of *Viscum album L.* (VA) medical effects is increasing, the role of its components is still unclear. VA extracts present several bioactive compounds as lectins and viscotoxins, which have been extensively described. However, there are few articles related to the investigation of the entire proteome of VA extracts [1]. The main problem in proteomic analysis is the isolation of proteins due to the wide range of concentration present in complex matrices. The most extended protein extraction protocols imply the use of phenol-based solutions or trichloroacetic acid-acetone [2]. Nevertheless, these methods are not selective and low abundance proteins remain masked by the high ones. For this reason, the use of alternative methods able to solve these problems is needed.

In this regard, the aim of this work is to go deep inside the proteome of VA extracts to understand its benefits in human health. For this purpose, three extraction methods have been conducted and meticulously compared. The first protocol implied the use of combinatorial peptide ligand libraries (CPLLs), which are able to reduce the dynamic protein range concentration by concomitantly decreasing the concentration of high-abundance proteins while increasing the trace ones. The second protocol was based on the use a solid-phase extraction (SPE) sorbent composed by a glycidyl methacrylate monolith modified with gold nanoparticles, in which proteins were isolated according to their isoelectric point. Finally, the third protocol implies the use of a commercial tip which selectively retains glycoproteins present in VA extracts. After protein extraction with the 3 protocols, eluates were subjected to SDS-PAGE and subsequently to HPLC-MS analysis. After identification of the VA proteome, the molecular functions of each eluate were evaluated and carefully compared.

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P-SP-10

MOLECULARLY IMPRINTED MACROPOROUS MONOLITHIC MATERIALS FOR SELECTIVE RECOGNITION OF HUMAN SERUM ALBUMIN

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Protein recognition assays have been used in separation, biosensors and clinical diagnosis fields. With the recent development of proteome techniques, the interest in finding biomarkers from human plasma for clinical diagnosis has gained new momentum. However, the wide dynamic range of protein abundance brings great challenges to discover low abundance proteins with significant biological functions. To recognize these analytes, the most extended methodologies require antibodies and enzymes, in which the preparation involves a considerable cost and effort. In the last years, molecular imprinting techniques, a type of artificial synthetic materials with specific recognition ability for target molecules, have strengthened as attractive approaches to address this issue [1]. However, most articles of molecularly imprinted polymers (MIPs) have focused on the recognition of small molecules, and scarce attention has been paid in the design of biomacromolecules imprinted polymers. Human serum albumin (HSA) is a large globular protein, which regulates the transport and availability of numerous chemical compounds in the blood vascular system. However, this protein represents 52-62% of the total plasma protein fraction, thus hindering the identification of other low abundance proteins. In this sense, several MIPs have been designed to capture HSA in biological samples, based on methacrylic acid (MAA) [2] or acrylamide monomers [3]. However, most experimental protocols to prepare the HSA-based MIPs are lengthy (e.g. hierarchical imprinting) or the polymers synthesized do not fulfill the flow-through properties required to be used as sorbent in solid-phase extraction (SPE) mode.

In this work, MIP materials, using 4-vinyl pyridine (VP) as functional monomer, have been synthesized by bulk polymerization to remove HSA from human serum. Several variables that affect the molecular recognition (such as template/VP/cross-linker ratio and extraction conditions) were optimized. In addition, the selectivity of the synthesized MIPs towards other proteins different from HSA was evaluated as well as its adsorption capacity, reproducibility and reusability. The material that offers the best performance was applied to the depletion of HSA from serum samples. The results demonstrated that the MIPs might become in effective artificial antibodies for the selective depletion of high abundance proteins.

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P-SP-11

APTAMER-MODIFIED MONOLITHIC CAPILLARY COLUMNS FOR HIGHLY SELECTIVE RECOGNITION OF ALLERGENIC PROTEINS

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Aptamers are single stranded DNA or RNA oligonucleotides that can be screened from a large random combinatorial nucleic acid library by systematic evolution of ligands by exponential enrichment (SELEX) according to their high affinity and specificity for various targets [1]. Thus, aptamers can be immobilized for the separation, preconcentration or detection of biomolecules as aptamer affinity chromatography [1]. The aptamers may be immobilized on the inner surface of fused silica capillary, microparticles, monoliths or microchips, among other chromatographic supports. However, a limitation of the open tubular capillaries is the small loading capacity because of the limited surface area of the inner wall. On the other hand, the packing of microparticles in column is labor intensive and troublesome, particularly for capillary chromatography. Due to these limitations, aptamer-modified polymer monolith is a choice of interest taking into account its well-known advantages such as rapid mass transfer, low back pressure, ease of preparation and functionalization.

The objective of this research was to develop an affinity aptamer monolithic capillary chromatography technique for protein separation and detection, taking advantage of both monolithic columns and aptamers. For this purpose, a series of biotinylated aptamers for capturing the major allergenic protein (*Ole e1*) found in olive tree pollen were immobilized on poly(glycidyl methacrylate) monolithic columns. The separation performance and selectivity (using other proteins such as human serum albumin and cytochrome c) of the aptamer affinity monolithic columns were evaluated. To our knowledge, this is the first study reported for selectively screening of *Ole e1* and it represents a great promise for a facile detection and diagnostic of this disease-related protein in several food extracts.

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P-SP-12

IMPROVING FRACTIONATION OF HUMAN MILK PROTEINS THROUGH CALCIUM PHOSPHATE CO-PRECIPITATION AND THEIR RAPID ANALYSIS BY CAPILLARY ELECTROPHORESIS

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Human milk has been settled as the best way of providing both full and preterm infants with the essential nutrients for a healthy growth and development. Within human milk constituents, the protein fraction plays a key role in achieving many of the beneficial outcomes of breastfeeding. Prior to their analysis, milk proteins are usually fractionated on acidification to pH 4.6 (the isoelectric pH), where coagulation of caseins occurs, and they precipitate readily out of solution (whey fraction). However, some whey proteins may co-precipitate with caseins at this pH and the other way around. In addition, this fractionation approach has been usually applied to bovine milk and in a lesser extent to human milk.

This work describes a simple sample pretreatment method for the fractionation of human milk proteins into their two main groups: whey and caseins, prior to their analysis through more sophisticated techniques. The protein extraction protocol is based on the addition of calcium and phosphate ions to non-adjusted pH human milk. The combination of calcium ions with phosphate results in an effective co-precipitation of caseins. To assess the suitability of this fractionation protocol, the protein extracts were analyzed by SDS-PAGE, LC-MS/MS and CE. The results evidence a significant decrease in contamination of casein fraction with whey proteins and vice versa compared with the conventional isoelectric precipitation of caseins. In addition, CE fraction collection coupled to LC-MS/MS (offline coupling) has been successfully applied to the identification of minor proteins in this complex matrix. The methodology presented here constitutes a promising tool to enlarge the knowledge of human milk proteome.

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P-SP-13

POLY(ETHYLENE GLYCOL) DIACRYLATE-BASED GROUND MONOLITHIC SORBENT FOR DETERMINATION OF SULFONAMIDES IN DIFFERENT MATRICES

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Antibiotics are widely used in livestock production with many purposes, such as disease treatment/prevention and to improve feeding efficiency. Nevertheless, the abuse of these drugs in food-producing animals could cause toxic effects, with direct impact on public health. For this, governmental agencies have set maximum residue limits for certain veterinary drugs in food [1]. Within antibiotic classes, sulfonamides have been extensively administered to food-producing animals, being their isolation and determination in different matrices, such as meat or milk. However, the analysis of these analytes remains a challenging task due to their low concentrations in complex matrices. To determine these antibiotics, analytical methods mainly based on HPLC coupled to mass spectrometry in tandem mode (LC-MS/MS) are commonly used [2]. In addition, efficient extraction and cleanup methods of sulfonamides for food analysis are required and have been reported in the last years (*e.g*. QuEChERS [3]). However, these protocols are time-consuming and offer a limited selectivity and reusability. To enhance these analytical properties, researchers have explored novel sorbent materials using polymeric monoliths [4]. In particular, monoliths based on poly(ethyleneglycol) diacrylate (PEGDA) have been successfully applied to the retention of polar aromatic molecules (such as sulfonamides) in capillary electrochromatography [5]. However, the extension of these highly cross-linked monoliths to solid-phase extraction (SPE) has not been yet explored.

In this work, a SPE sorbent based on PEGDA ground monolith has been synthesized and used to selectively extract several sulfonamides from food matrices. Several extraction parameters influencing the analytical performance were established. The optimized procedure was applied to the determination of sulfonamides in meat tissues and milk. In addition, some validation parameters (linearity, limits of detection and quantification and precision) have been evaluated. To the best of our knowledge, the preconcentration achieved with our SPE methodology will have a wide field of application.

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P-SP-14

DEVELOPMENT OF MINIATURIZED SYSTEMS BASED ON POLYMERIC SORBENTS MODIFIED WITH GOLD NANOPARTICLES FOR AMINOTHIOLS ANALYSIS IN BIOLOGICAL SAMPLES

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Amino thiols are biochemically very active organic compounds, being involved in several biological processes. Thus, the altered levels of these thiols (e.g. decreasing glutathione (GSH) concentrations) in plasma may be implicated in aging and the pathogenesis of many diseases, such as rheumatoid arthritis, muscular dystrophy, and Alzheimer's disease [1]. Then, the accurate measurement of aminothiols, particularly in GSH and homocysteine, in biological fluids is an important task for the diagnosis of these serious diseases.

Preconcentration and cleanup of biological samples is usually a pretreatment step required to reach the low levels found for these compounds in these matrices. In the last years, gold nanoparticles (AuNPs) have been shown to be very effective sorbents for the extraction of thiol-containing compounds as a result of the formation of Au–S bonds [2]. However, most of these methodologies based on dispersive liquid microextraction showed certain limitations such as losses of nanomaterial occurred during washing or centrifugation steps. In this sense, solid-phase extraction (SPE) based on polymer monoliths modified with AuNPs [3], which have been successfully tested for macromolecules isolation, can represent a promising alternative to overcome these actual drawbacks in analysis of aminothiols.

In this work, polymeric sorbents based on glycidyl methacrylate were prepared into a syringe device, and applied to isolate aminothiols in several biological samples. The prepared material was evaluated as SPE sorbent. Several extraction parameters and other variables (breakthrough volume and reusability) influencing on the analytical performance were established. After the SPE, HPLC-DAD analysis of these analytes was carried out [4]. The optimized protocol was applied to the determination of the GSH and other relevant aminothiols in saliva, urine and plasma samples.

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P-SP-15

A MODIFIED QUECHERS METHOD FOR THE DETERMINATION OF TETRACYCLINES IN FISH MUSCLE BY UHPLC–MS/MS

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Fish is one of the most consumed products in the world due to the changes in eating habits in the last decades. In this sense, aquaculture provides the possibility of producing larger quantities of products in reduced space, being an emerging industry. However, large-scale fish production leads to a higher concentration of animals in small spaces and substantially increases the risk of diseases. In this scenario, the use of antibiotics is a common practice, due to is an effective way of treating and preventing infections. Among others, tetracyclines (TCs) are a class of broad-spectrum antibiotics widely used in aquaculture. The main risks of this misuse are allergies, toxic effects or the appearance of bacterial resistance. In order to protect human health, a maximum residue limit (MRL) for TCs in fish muscle of 100 μg kg^{-1} has been established by the European Union. This entails the development of rapid, sensitive and direct analytical methods to support the control on their presence and behavior in fish, so as to ensure the safety for consumers.

Bearing in mind these reasons, in this work a sample treatment based on a modified QuEChERS method combined with ultra-high-performance liquid chromatography–tandem mass spectrometry (UHPLC–MS/MS) was proposed to determine the residues of five common TCs in fish muscle samples. The separation was achieved in less than 4 min and the analytes were detected in electrospray ionization in positive mode (ESI+) with multiple reaction monitoring mode (MRM). Parameters affecting the extraction step, such as the amount of sample and EDTA-McIlvaine buffer and extraction solvent volumes, were optimized by means of experimental design. In order to obtain the lowest matrix effect, parameters affecting the clean-up step by dispersive solid phase extraction (dSPE), were also studied. Under optimum conditions, matrix effect was lower than |15|% in all cases. Limits of quantification were lower than 4.4 μg kg^{-1} for the compounds in the selected samples, being in compliance with the current legislation. The precision, expressed as relative standard deviation, was below 18.5% and the recoveries for fortified fish samples (salmon and panga) higher than 80%. These results revealed that the proposed method is simple, rapid, cheap and environmentally friendly, being successfully applicable for the determination of these residues in fish samples.

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P-SP-16

OPTIMIZATION OF THE EXTRACTIONS BY SUPERCRITICAL FLUIDS AND PRESSURIZED LIQUID EXTRACTION FROM DATE FRUIT

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The date palm *Phoenix dactylifera*, a tropical and subtropical tree, belonging to the family Palmae (Arecaceae) is one of mankind's oldest cultivated plants. Date palm has long been one of the most important fruit crops in the arid regions of the Arabian Peninsula, North Africa, and the Middle East. Dates are a major food source and income source for local populations in the Middle East and North Africa, and play significant roles in the economy, society, and environment in these areas. [1]. Date fruits have gained great importance in human nutrition owing to their rich content of essential nutrients and various biological activities (hepatoprotective, anti-genotoxic, nephroprotective, anti-allergic, neuroprotective, antiviral, antifungal [2].

The aim of this work is to figure out set up a sample preparation method to address the composition and to explore the different activities of dates (fruit and seed) by using "green" extractions methods and to assess the differences between the varieties coming from different localities.

From the seeds, oil has been extracted by a supercritical CO_2 and analyzed by GC-MS. To set up the extraction conditions to have the best extract, a chemometric optimization was done. Different ranges of pressure (100-300 bar), temperature (40-80°C) and co-solvent (Ethanol: 0-10%) were chosen, then a statistical analysis was done to determine the optimum conditions (100 bar, 40°C and 10% ethanol). The oil of each extract obtained was analyzed by gas chromatography to determine the profile in fatty acids. The main fatty acid found in all the varieties was myristic acid (C14:0).

From the pulp the extraction was operated by Pressurized liquid extraction (PLE). The same methodology of optimization has been used; the variables were temperature (50-150°C) and solvent composition (Ethanol 100%, water 100%, water/Ethanol 50%). To get the optimum conditions an antioxidant assay was run and the yield was evaluated and then analyzed by the same method as SFE. The optimum was determined at those conditions of temperature: 150°C and Ethanol: 72%. Then the extracts were analyzed by HPLC-MS/MS.

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P-SP-17

CLOUD POINT EXTRACTION FOR DETERMINATION OF VITAMIN D AND THEIR METABOLITES IN HUMAN URINE USING LIQUID CHROMATOGRAPHY WITH TANDEM MASS SPECTROMETRY

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The two main forms of vitamin D, cholecalciferol (vitamin D_3) and ergocalciferol (vitamin D_2), are biologically inactive. While the first one is synthetized by our own organism by exposure to solar radiation, the second must be added in the diet. Both compounds are transformed in the organism by hydroxylation reactions [1]. Vitamin D contributes to the calcium and phosphorus levels regulation in the organism, being crucial to avoid diseases like osteoporosis [2]. Therefore, the control of their levels in biological fluids is of great importance.

In this work, cholecalciferol, ergocalciferol, their monohydroxylated metabolites (25(OH)D_2 and 25(OH)D_3) and their glucuronide metabolites were analyzed in urine samples by cloud point extraction (CPE) using liquid chromatography-tandem mass spectrometry (LC-MS/MS) with a triple quadrupole (QqQ). A procedure was developed to distinguish the free contents of the vitamers (D_2, D_3, 25(OH)D_2, 25(OH)D_3) and the total content of vitamin D which also includes the glucuronide metabolites. To measure the total content of vitamin D, it was necessary to perform an enzymatic hydrolysis to convert the glucuronide vitamin D into the free vitamin. The procedure, for total content analysis, consisted on the addition of 1 mL of 8000 U mL^{-1} of β-glucuronidase enzyme solution prepared in sodium acetate buffer (0.1 M, pH 5) to 8 mL urine. After incubating at 37 ºC for 2 h, this solution was diluted to 10 mL with water in the presence of 0.25 g NaCl, and preconcentrated by CPE by adding 200 µL of a 15% m/v Triton X-114 solution. The mixture was manually stirred and heated in a microwave oven at a power of 250 W for 20 s, in order to get the cloud point temperature of the surfactant. The sedimented phase obtained after centrifugation was diluted with 100 µL of methanol, in order to decrease its viscosity, and 20 µL were injected into the LC-MS/MS.

The use of non-ionic surfactants as extractants solvents permits higher transfer efficiency complying with the principles of green analytical chemistry. The precision of the method provides mean RSD values of 8% for repeatability. No matrix effect was observed, so quantification of samples was carried out using aqueous calibration. The limits of detection were between 0.2 and 0.8 ng mL^{-1}, depending on the compound. The developed method was validated by recovery studies, satisfactory values being obtained (83-120%) at three concentration levels. The metabolite 25(OH)D_3 was not detected in the urine samples, whereas D_2, D_3 and 25(OH)D_2 were found in their glucuronide forms at concentration levels in the 0.86-3.14 ng mL^{-1} range for D_2 and D_3 and in the 12.7-26.2 ng mL^{-1} for 25(OH)D_2.

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P-SP-18

SUPERCRITICAL FLUID EXTRACTION AND CHEMICAL CHARACTERIZATION OF TERPENES OBTAINED FROM OLIVE LEAVES

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The valorization of the biological waste generated both in the agricultural activity and in the processing industries has become a challenge for science, which seeks to investigate new alternatives for the sustainable management of the growing waste generation. The olive oil industry has an economic, commercial and industrial relevance in Spain, olive leaves being one of the main by-products, which are a natural source of bioactive phenols, secoiridoids, flavonoids and terpenoids. Several researchers point to olive leaves as a source of terpenoids, with structures ranging from C10 to C40 and several biological activities [1,2,3].

Alzheimer´s disease (AD) is known as a multifactorial neurological pathology. One of those factors is related with Acetyl Choline Estearase (AChE) activity responsible for the development of AD. This work was oriented towards the valorization of olive leaf through the systematic and selective extraction of the different families of bioactive terpenoids with potential anti AChE activity as a therapeutic approach in delaying the detrimental effects of AD.

Thus, for the isolation of low molecular weight terpenoids (C10-C15), CO_2 was used as pure solvent, working at low pressure values (80-120 bar). The extracts obtained at different SFE conditions were characterized GC-Q-TOF-MS. The results showed the presence of a wide variety of terpenic structures at different concentration levels according to the applied extraction conditions. Thus, operating at 120 bar during short extraction times (20-40 min), higher levels of monoterpenes (e.g. limonene, anethol, eugenol, thymol) were obtained. Subsequent extraction steps were carried out using co-solvents at higher pressure values to isolated higher molecular weight terpenoids such as Caryophyllene, Phytol, tocopherols, Uvaol, Stigmasterol and β-Amyrin, among others.

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P-SP-19

EVALUATION OF NEW PROTEOLYTIC ENZYMES TO PRODUCE HYPOCHOLESTEROLEMIC PEPTIDES FROM OLIVE SEED PROTEINS

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Hyperlipidemia, which is a key risk factor of cardiovascular diseases, has become a worldwide problem in the last decades due to a non-healthy lifestyle. Many synthetic drugs have been developed to treat hyperlipidemia but side effects derived from their long-term consumption have been described. At this regard, different natural compounds have been used for treating this disease when cholesterol and triglycerides levels are moderate. Olive seeds are a cheap source of proteins from which we can obtain bioactive peptides [1]. Particularly, peptides obtained by hydrolysis of olive seed proteins with Alcalase have shown capacity to *in vitro* reduce cholesterol and triglycerides [2].

The aim of this study was to evaluate the capacity of new proteolytic enzymes for the production of highly bioactive hydrolysates from olive seeds proteins. These enzymes normally comprise different isoforms that can differ in their proteolytic activity being necessary their previous characterization to select the most active one. Capillary electrophoresis coupled to mass spectrometry (CE-MS) is a powerful technique for intact proteins analysis [3]. Recently, Haselberg *et al.* demonstrated the usefulness of a prototype sheathless CE-MS for the efficient and repeatable analysis of intact proteins [4]. Besides, sheathless CE-ESI-MS is ideally suited for characterizing enzymes and their different isoforms.

Protein isolates from olive seeds were hydrolysed by 7 different proteolytic enzymes and the hypocholesterolemic activity of these hydrolysates was evaluated by three different mechanisms: capacity to reduce the cholesterol micellar solubility, capacity to inhibit cholesterol esterase, and capacity to inhibit lipase pancreatic. The enzyme which produced the most hypocholesterolemic peptides was characterized by CE-ESI-MS. Finally, the hydrolysis with the most active isoform was optimized and the hypocholesterolemic capacity of obtained peptides was compared with the obtained using commercial enzymes.

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P-SP-20

AUTOMATION OF SINGLE-DROP EXTRACTION APPROACHES BASED ON THE LAB-IN-SYRINGE TECHNIQUE

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The Lab-In-Syringe (LIS) technique [1] is a flow-batch technique using the void of a syringe pump as a mixing and reaction chamber with adjustable volume. The technique gains versatility by adding a magnetic stirring bar inside the syringe void and a device for forming of magnetic field to induce rotation [2]. Homogenous mixing of the aspirated solutions is achieved in this way, unlike in other flow techniques, where zone overlapping by dispersion is the main phenomena for solution mixing. This makes the LIS technique ideally suited for the automation of liquid-liquid microextraction and dispersive liquid-liquid microextraction [3].

Since its introduction in 1995, single-drop microextraction (SDME) [4] has developed into a widely used sample pretreatment methodology. Several modes are known up-to-date with drop formation in headspace (HS-SDME), directly immersed (DI SDME), or in continuous flow as the most common ones.

Performing SDME manually is a tricky task, especially considering drop stability and reproducibility of drop formation, retraction, and transfer to a detection device using microsyringes.

The exploitation of the advantageous features of LIS for automation SDME approaches is overviewed here. HS-SDME and DI-SDME were used for the analysis of food and environmental samples. Ethanol in wines was determined with HS-SDME, based on the reduction of a drop of dichromic acid by the volatile analyte. For ammonia determination in river waters, a novel, double-orifice syringe was used for the first time allowing on-drop sensing during the extraction. Finally, lead in drinking water was extracted into a directly immersed drop of solvent mixture after complex formation with dithizone.

Solutions to technical issues as well as optimization of chemical and physical parameters are explained. The achieved results comprising adequate analyte recovery, limits of detection and reproducibility for to the application to real samples analysis will be detailed.

Acknowledgements: This work was supported by the STARSS project (Reg. No. CZ.02.1.01/0.0/0.0/15_003/0000465) co-funded by ERDF. The authors also acknowledge the support of the Czech Science Foundation through project No. 17-08738S.

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P-SP-21

MINIATURIZED DISPERSIVE SOLID-PHASE EXTRACTION USING A NOVEL METAL-ORGANIC FRAMEWORK CIM-81 AS SORBENT FOR THE EXTRACTION OF PERSONAL CARE PRODUCTS IN ENVIRONMENTAL WATERS

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Personal care products (PCPs) are a group of emergent contaminants included in a wide number of dairy products for human cleaning such as gels, lotions, and cosmetics [1]. There are mainly six groups of PCPs: UV filters, preservatives, disinfectants, musk, insect repellents, and siloxanes; some of them even designated as endocrine disrupting chemicals with high toxicity. The direct or indirect human exposure to PCPs is unavoidable due to the continuous incorporation of PCPs into the environment.

The monitoring of PCPs in environmental samples requires sample preparation to ensure proper preconcentration, considering their low levels and the complexity of the environmental samples. Trends in green analytical chemistry advice the development of miniaturized and fast methods while maintaining an adequate analytical performance in terms of accuracy, sensitivity, and reproducibility. Among recent environmental friendly techniques, the miniaturized dispersive solid-phase extraction (D-µSPE) highlights by its simplicity (addition of the sorbent to the liquid sample, followed by agitation to favor the partitioning of the analytes to the sorbent, and then separation of the sorbent containing the trapped analytes and further analytical determination). D-µSPE also requires low amounts of solid sorbent (< 500 mg), while implying short analysis times and high enrichment factors. Trends also focus on the search of novel and more efficient sorbent materials for D-µSPE.

Metal-organic frameworks (MOFs) are microporous crystalline polymers formed by inorganic units and organics linkers joined through coordinated bonds [2]. The unique and excellent characteristics of MOFs (tuneability, porosity, high thermal and chemical stability, together with the highest surface areas known) have aroused the scientific interest for their use in analytical sample preparation.

This study proposes the utilization of a novel MOF, CIM-81, as sorbent in D-µSPE for the determination of a group of PCPs in environmental water samples, followed by ultra-high performance liquid chromatography and ultraviolet detection.

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P-SP-22

NOVEL METAL ORGANIC FRAMEWORK-BASED SOLID-PHASE MICROEXTRACTION FIBERS: IMPORTANCE OF SUPPORT TREATMENT

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Solid-phase microextraction (SPME) is a powerful analytical sample preparation method that utilizes fiber coatings as the key device for its performance. It has a number of advantages such as robustness, high thermal and chemical stability, simplicity, fastness, and impressive sensitivity, while being an organic solvent-free procedure (and thus environmental-friendly) in the majority of the cases. Recent trends in the SPME field focus on the development of new coating materials to increase the versatility, the selectivity and/or the extraction efficiency of the technique. Among novel coatings with outstanding properties, metal-organic frameworks (MOFs) merit citation [1]. MOFs are porous coordination polymers composed by metal ions and organic linkers, characterized by their crystallinity and by the highest surface areas known. They have accessible cages, tunnels and modifiable pores, together with adequate chemical, mechanical, and thermal stability.

The preparation of MOF-based SPME coatings implies proper growing of a crystal onto a metallic support. Therefore, proper pretreatment of the fiber support is mandatory to ensure the obtaining of robust MOF-based SPME coatings. The type of pretreatment used is going to determine the nature of the linkage between the support and the MOF.

The main objective of this study is the development of a new coating for SPME based on the MOF ZIF-8, ensuring robustness of the coatings while applying novel bonding approaches and thorough characterization [2]. Furthermore, as-prepared SPME coatings should prove analytical performance in the direct immersion (DI-) or headspace (HS-) SPME for a variety of contaminants and in combination with gas chromatography.

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P-SP-23

MINIATURIZED DISPERSIVE SOLID-PHASE EXTRACTION *VERSUS* MINIATURIZED STATIC SOLID-PHASE EXTRACTION USING AS SORBENT CORE-SHELL MICROPARTICLES OF THE METAL ORGANIC FRAMEWORK CIM-80 (CIM-80@SiO_2) FOR THE EXTRACTION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM WATERS

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Green analytical chemistry has become a hot topic nowadays. The main idea of this trend is to reduce the environmental impact caused by conventional analytical procedures. Miniaturized solid-phase extraction (µSPE) is a sample preparation technique requiring low amounts of solid sorbent (<500 mg). There are three main modes to perform the extraction: static, dispersive (D-µSPE), and magnetic-facilitated dispersive (M-D-µSPE). In the static mode, the solid sorbent is confined into a device and sample passes through it. In the D-µSPE mode, the sorbent material is added and dispersed into the sample solution [1].

Metal-organic frameworks (MOFs) are crystalline materials full of cavities that makes them have the highest surface area known. Furthermore, MOFs present several interesting properties such as high adsorption affinity, uniform pore topologies, good thermal and mechanical stability, and easy structural tuneability. Given these properties, it is not surprising that MOFs have captured scientific community attention in analytical sample preparation [2].

In this study, MOF@silica core-shell microparticles, using the novel MOF CIM-81, are screened in D-µSPE and static µSPE towards environmental water analysis (for determining polycyclic aromatic hydrocarbons), while comparing their analytical performance behavior with neat silica microparticles.

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P-SP-24

UNSUPERVISED IN-VITRO MONITORING OF THE LEACHING KINETICS OF EMERGING CONTAMINANTS FROM MICROPLASTICS IN THE MARINE ENVIRONMENT BY ON-LINE COUPLING OF MINI-COLUMN EXTRACTION TO HPLC

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Microplastics are submillimeter particles of polymeric nature produced as a consequence of the human industrial / social activity. While they can be produced intendedly because of their many benefits and properties (primary microplastics), they can also be generated from climatologic weathering of plastic substances released to the environment (secondary microplastics). Those microplastics accumulate in the marine environment where they have been proven to hinder life sustainability because of the mechanical / physical interference in physiological processes. However, the chemical contribution to life hindrance due to leaching of constituent monomers / oligomers, plastic additives or sorbed species has not yet been proven, even if the impact in the ecosystem may be higher due to (i) the larger number of living organisms exposed, (ii) the potential direct interference in metabolic processes, and (iii) the unintentional entry into food chain. Many of the potential leachable substances are currently being considered emerging pollutants.

In this contribution, we present a fully automatic flowing stream system combining dynamic bioaccessibility testing with on-line extract processing as a front end to HPLC for assessing the leachability of phthalates and bisphenol A in seawater using certified materials of polypropylene and polyvinyl chloride microplastics. The sampling / pretreatment part is composed merely of two syringe pumps and a rotary selection valve that allow in a fully automatic mode to (i) leach the sample dynamically with seawater, (ii) process the extracts on-line, (iii) perform internal calibration and (iv) effect quality control assays. The flow manifold is online hyphenated to HPLC-PDA through the switching valve approach (using a monolithic column as online preconcentrator) for separation and quantification of the target analytes. The flow system is computer controlled and synchronized with the HPLC run by the CocoSoft automation suite for unsupervised operation. Results indicate that only analytes with Log Kow < 4.5 are significantly leached due to the action of seawater.

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P-SP-25

EVALUATION OF IN-HOUSE SYNTHESIZED POLYMERIC SORBENT WITH ZWITTERIONIC CHARACTER FOR THE SIMULTANEOUS SOLID-PHASE EXTRACTION OF ACID, BASIC AND AMPHOTERIC ANALYTES.

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In the present study, an in-house synthesized weak cation-exchange and weak anion-exchange zwitterionic sorbent for solid-phase extraction (SPE) has been developed and evaluated for the retention of acid, basic and amphoteric analytes simultaneously. A tertiary amine and a carboxylic acid are the cationic and anionic moieties attached to the WAX/WCX sorbent, respectively. The synthesis of the sorbent first consisted of the preparation of the hypercrosslinked polymer.in order to achieve high specific surface area. The functionalization of the polymer was performed using sarcosine ethyl ester hydrochloride to introduce the anion-exchange properties to the particles. The subsequently hydrolysis of the ester groups allowed the polymer to acquire the cation-exchange properties [1].

Different SPE parameters were optimized and thoroughly discussed so as to get the optimum extraction conditions, such as the amount of sorbent placed into the cartridge, the loading pH, the washing volume and the elution solution. Special attention was paid to the pk_a values of the analytes and the functional groups of the sorbents in order to promote effective interactions between them [2]. Eventually, 200 mg of the synthesized sorbent were packed into the SPE cartridge. The loading pH was set at pH 3 and 6. After loading the solutions, a washing step was introduced consisting of 1 mL of MeOH. The elution step was performed with 5 mL MeOH containing 5% NH_4OH.

The optimized SPE followed by liquid chromatography-high resolution mass spectrometry (Orbitrap) was successfully applied to determine the 11 model compounds selected from different type of complex environmental water samples.

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P-FCH-01

DEVELOPMENT OF A RETENTION TIME INDEX FOR LIQUID CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY IN BOTH POSITIVE AND NEGATIVE IONIZATION MODES

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The accuracy and sensitivity of high resolution mass spectrometry (HRMS) enables the identification of candidate compounds with the use of mass spectrometric databases among other tools. However, retention time (RT) data in identification workflows has been sparingly used since it could be strongly affected by matrix or chromatographic performance. Retention time index (RTi) strategies can provide a more robust and valuable information than RT, gaining more confidence in the identification of candidate compounds in comparison to an analytical standard. Up to our knowledge, no RTi has been developed for LC-HRMS systems providing information when acquiring in either positive or negative ionization modes.

An RTi strategy has been developed by means of the use of 16 isotopically labelled reference standards, which can be spiked to a real sample without resulting in possible false negatives.

For testing the RTi performance, a mixture of several reference standards, emulating suspect analytes, has been used. RTi values for these compounds were calculated both in solvent and spiked to a sample to assess the effect of either chromatographic parameters and/or matrix in different scenarios. It has been demonstrated that the variation of injection volume, chromatographic gradient and initial percentage of organic solvent injected does not considerably affect RTi calculation. Column aging and solid support of the stationary phase of the column, however, showed strong effects on the elution of several test compounds. Yet, RTi permitted the correction of elution shifts of most compounds. Finally, RTi has been tested in 47 different matrices from food, biological, animal feed and environmental origin. The application of RTi in both positive and negative ionization modes showed satisfactory results for most matrices studied.

The RTi developed can be used in future LC-HRMS screening analysis giving additional information, which facilitates tedious processing tasks and gain more confidence in the identification of (non)-suspect analytes.

P-FCH-02

ADVANTAGES OF PARAFAC DECOMPOSITION IN THE UNEQUIVOCAL IDENTIFICATION AND QUANTIFICATION OF PLASTICIZERS AND BENZOPHENONE MIGRATED FROM FOOD CONTACT MATERIALS BY GC/MS

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The migration of chemicals from food contact materials into food is an important issue in food safety to ensure the protection of human health and the interests of consumers. Tenax has been established in Regulation (EU) No 10/2011 [1] as food simulant E for testing specific migration from plastics into dry foodstuffs.

In this work, the migration of four plasticizers and benzophenone (BP) from polypropylene (PP) coffee capsules and a paper bread bag into Tenax as food simulant was studied by means of gas chromatography/mass spectrometry (GC/MS) and PARAFAC. The four plasticizers were: butylated hydroxytoluene (BHT), diisobutyl phthalate (DiBP), bis(2-ethylhexyl) adipate (DEHA) and diisononyl phthalate (DiNP), being DiBP-d_4 the internal standard. BP is an ultraviolet (UV) stabilizer used in food applications.

The samples measured for the analysis of each food contact material were arranged in data tensors and PARAFAC or PARAFAC2 decompositions were performed. An unidentified interferent present in the migration samples of the coffee capsules appeared in the PARAFAC models for all the analytes. The baseline appeared as another factor in these models for BP, DEHA and DiNP. In the case of the analysis of the paper bread bag, an unidentified interferent coeluted with BP. PARAFAC and PARAFAC2 decompositions enabled the unequivocal identification and determination of all the analytes despite some of the m/z ratios of the interferents were shared with the analytes. Otherwise, the presence of the analytes could not have been ensured according to the regulations currently in force [2]. In addition, PARAFAC has dealt with finger-peak chromatographic signals such as that of DiNP.

Trueness was verified at a 95% confidence level in all cases and the amount of BP and DiBP migrated from the PP coffee capsules was 46.45 μg L^{-1} and 13.11 μg L^{-1}, respectively, whereas none of the analytes were detected in the analysis of the bread bag.

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P-FCH-03

PULSES OF ORGANIC SOLVENT AND THEIR CONSEQUENCES TO ENHANCE ISOCRATIC AND GRADIENT PREDICTIONS

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Multi-linear gradients constitute an excellent alternative in the resolution of complex samples by HPLC, owing to its flexibility to accommodate the requirements of all constituents. In the search of the best separation, the presence of solutes of close properties promotes optimal gradients often including low slope segments, followed by strong changes in the organic solvent content. The presence of such sudden changes gives rise to deficient predictions, which may compromise the reliability of a systematic optimization.

When a change in the composition of the mobile phase (i.e., a gradient change, or a pulse) reaches the column inlet, its effects always take a certain additional time to reach the solute neighborhood, owing to the distance travelled by the solute from the inlet. Thus, the instant composition experienced by the solute includes two delays: one of them is the dwell time (associated to the path travelled by the mobile phase from the mixer to the column inlet), and the second, not included in the literature treatments, is the above internal delay. Naturally, with the solute displacement, the magnitude of the delay increases, and the need for correction is more mandatory.

This work studies the improvements of predictions in retention time, in the presence of extreme variations in organic solvent, implementing the internal delay explained above. For this purpose, several experiments were designed, eluting a set of ten sulfonamides in the presence of pulses of organic solvent. These pulses were gradually shifted to affect the sample components in a varying extent. In these conditions, very important errors can occur in the prediction of retention. Thus, solutes eluting immediately after the pulse would pass from moving very quickly to be practically steady as their hydrophobicity increases. In addition, they suffer important drops in efficiency in the region right after the pulse.

Pulses also constitute an interesting possibility in experimental designs to have access to measurements at low concentration of organic solvent. These compositions are normally inaccessible in isocratic mode. In a pulse, however, the transitory presence of a high concentration of solvent for a short time gives rise to measurable retention times, where the low concentration of organic solvent has still a certain weight. The performance in modelling terms of mixed designs (including isocratic and/or gradient experiments, together with pulses), for obtaining more informative sets of experiments, is explored.

P-IP-01

CHROMATOGRAPHIC FINGERPRINT OF WOOD PROCESSING INDUSTRY BY-PRODUCTS: EUCALYPTUS, OAK AND CHESTNUT SCREW WATERS

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The manufacture of wooden hardboards and fibreboards is distinguished in some companies -as *Betanzos HB*- by the non-use of artificial adhesives to join wood fibres, using water instead. This aspect converts the different by-products of the industrial process into highly attractive sources of the bioactive compounds that are originally in the raw materials, which on the other hand, come from sustainable forests. These by-products of wood processing, named concentrates, condensates and screw waters, could be reused in this way, reducing the environmental impact of the industrial activity and obtaining, in parallel, an economical profit.

Screw waters derived from the transformation processes of eucalyptus (*Eucalyptus globulus*), oak (*Quercus robur*) and chestnut (*Castanea sativa*) woods are comparatively characterized in this work. Physical, mechanical and chemical characteristics of the raw materials are first determined, along with the basic physico-chemical parameters, the total polyphenolic content and the antioxidant capacity of the corresponding byproducts and/or derived extracts.

Based on gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis, the chromatographic fingerprints have been additionally obtained in order to identify the main extractable organic wood components: terpenes, terpenoids and phenolic compounds. Solid-Phase Microextraction (SPME) was also used to characterize the most volatile compounds. The ultimate target is to obtain derived products useful as additives in the food industry.

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P-IP-02

SEARCHING BIOACTIVE COMPOUNDS IN WOOD INDUSTRY BY-PRODUCTS: WOODEN CHIPS FROM PINE, WALNUT AND CHERRY

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Wooden chips are co-products of the wood processing industry that come from the first step in the production process of fibreboards, the chipper. Looking for complementary ways of reassessment of such industrial byproducts in order to minimize the environmental impact of the industrial activity, simple extraction approaches have been applied to get extracts rich in bioactive compounds ready to use in other industrial sectors, such as cosmetics or alimentary. The species evaluated were pine (*Pinus pinaster*), walnut (*Juglans regia*) and cherry (*Prunus avium*). Previous studies have already shown the presence of bioactive compounds in walnut (melatonin, serotonin and polyphenols) [1], cherry (sugars, organic acids and phenolics) [2] and pine (mainly simple phenolics, stilbenes, flavonoids and lignans) [3], but the use of wooden chips as raw material has not been formerly evaluated.

The aim of this study is to assess a simple and environmentally friendly solid-liquid extraction procedure, with and without temperature, in order to extract the organic compounds with potential bioactivities present in the water in contact with the different wooden chips. The scaling up of the extraction process on a medium and industrial scale will be evaluated, looking for a possible quick, simple, effective and economical implementation in the industrial wood processing facilities. Extracts were analyzed by gas chromatography-mass spectrometry (GC-MS) and by liquid chromatography-tandem mass spectrometry (LC-MS/MS) in order to evaluate the presence of volatile and non-volatile organic compounds, to find bioactive compounds from either type.

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P-NDI-01

TARGETED AND UNTARGETED SCREENING OF PESTICIDES AND OTHER CONTAMINANTS IN FOOD MATRICES USING A NOVEL HIGH RESOLUTION GC/Q-TOF

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Due to the large number of potential pesticide residues and metabolites present in food products, fast and reliable analytical methods for the screening, identification and quantification of pesticides in low levels and in a broad range of food matrices are needed. Criteria for the identification of analytes and confirmation of results are defined in the guidance document SANTE/11945/2015 and require the presence of two ions including a fragment for each compound with a good mass accuracy.

In this study, we demonstrate a novel GC/Q-TOF based workflow for targeted, suspect and unknown screening in two example matrices (grape and onion). The samples were analyzed by full scan GC/Q-TOF with a mid-column backflushing configuration and a 20 minute retention time locked (RTL) method.

The results demonstrate that the combination of high resolution accurate mass GC/Q-TOF and an accurate mass library serve as an effective and robust tool for qualitative and quantitative targeted screening of pesticides. A great majority of spiked pesticides were identified at all five spiking levels with good mass accuracy < 5 ppm. The novel data acquisition system enabled a linear response of those pesticides over a wide concentration range, yielding linear calibration curve fitting coefficient (R 2) of ≥ 0.99 in the matrix matched calibration from 5 to 100 ng/mL. The repeated experiments also yielded stable ratio of fragment ion abundance, with small variations observed. The mid-column backflushing method resulted in good instrument precision, with standard deviation (SD) of retention time ≤ 0.01 min for most identified pesticides obtained for >100 pesticides. The untargeted screening of those food matrices enabled the investigation of other contaminants in the matrices

Topics: GC–Q/TOF, high resolution, pesticide screening

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P-NDI-02

LAB-IN-SYRINGE: A YOUNG AND POWERFUL TECHNIQUE FOR AUTOMATION OF SAMPLE PRETREATMENT

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Since the first proposal of the *Lab-In-Syringe* (LIS) technique in 2012 [1], also referred to as *In-Syringe Analysis*, this flow-batch automation approach is wide spread and is currently the subject of analytical research and development.

The basic system is assembled from an automated syringe pump and selection valve, i.e. simple and compact instrumentation, which is available in most laboratories and which resembles in principle the apparatus of its parental technique *Sequential Injection Analysis* (SIA) [2]. In contrast to SIA operation, based on solution stacking and mixing by dispersion, the syringe void itself is employed to carry out mixing processes and chemical reactions.

The LIS technique has gained even more versatility by engaging a magnetic stirring bar inside the syringe to enable homogeneous mixing and liquid phase dispersion [3], using the syringe upside-down for phase inversion [4], taking advantage of the transparency of the syringe and use as detection cell [5], or additional inlet via the piston [6].

LIS has demonstrated efficient and advantageous over other flow techniques for the automation of multiple sample pretreatment procedures including dispersive liquid-liquid phase microextraction, dispersive solid phase extraction, headspace (singe-drop) extraction, or cloud point extraction [7,8].

We strongly believe that the potential of this technique is far away from been fully explored. In this poster, we give a graphical overview of the potentials of this technique, operation modes, and devices required to set up a Lab-In-Syringe analyzer and a closer look on tricks and technical limitations is given, aiming for further use and distribution of this technique.

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P-NDI-03

UNIQUE GC COLUMN SELECTIVITY FOR TIME AND COST-EFFICIENT SEPARATION OF COMPLEX CIS/ TRANS FATTY ACID METHYL ESTERS IN FOOD

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Increased resolution and efficiency are every analytical chemist's desire. Though a 60 minute analytical run has traditionally been common for analysis of fatty acid methyl esters (FAMEs) due to their unique structures, analysts in production environments often need faster run times to improve productivity. Using several key GC column parameters including selectivity and dimensions, run time for a typical 37 component FAMEs sample can be reduced to as short as 12 minutes. Using a high cyano Zebron™ ZB-FAME GC column, demonstration of successful tactics for achieving short, successful FAMEs testing methods for real food samples is explored.

P-NDI-04

STATIONARY PHASES FOR THE PROCESS SCALE PURIFICATION OF PEPTIDES AND INSULIN ANALOGS

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The development of a multi-step purification process on two types of silicas is presented here for a commercially significant crude insulin analog, Insulin Glargine. The focus is to demonstrate the efficacy of both prep C8 phases on a well-established USP method that has been further optimized on the analytical format and then scaled to the prep format to produce material of a suitable purity. The investigative parameters include base silica and gradient conditions.

P-OT-01

OIL QUALITY ASAP: DETECTING DEFECTED AND ADULTERATED OILS BY DIRECT MS USING ATMOSPHERIC SOLIDS ANALYSIS PROBE

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Olive oil quality is a matter of concern for consumers and producers. It establishes the differences between low value products with poor attributes and products with outstanding features, and, consequently, it contributes to set oil prices. This classification, as established by Spanish and EU legislations, is performed by testers who establish if an olive oil must be labelled as extra virgin, virgin or lampante (not recommended for consumption). This strategy is known as "PANEL TEST", which classifies the oils according to two main properties: defects and good attributes.

According to the literature [1,2], the organic compounds responsible of these attributes have been determined to be predominantly volatiles, including esters, ketones, aldehydes, alcohols, terpenes, phenols and their derivatives, with different concentrations and odour thresholds. Taking this into account, a more objective methodology, based on instrumental responses, could be presented as an alternative approach to PANEL TESTs interesting for the olive oil industry. Also, this could be useful as a complementary tool to prevent fraud due to sample adulteration. In this work, the capabilities of direct mass spectrometry (MS) making use of an Atmospheric Solids Analysis Probe (ASAP) have been tested for the determination defected and adultered olive oils. The ASAP source vaporizes solid and liquid samples using a high temperature nitrogen flow, with minimal or no simple treatment at all. In this case, 200 mg of oil were diluted in 1mL of acetone with triphenyl phosphate as internal standard. Later, one drop of the sample is taken with a glass capillary and vaporized in the ASAP source. All the samples were analyzed by duplicate along with QCs (pool of all samples) every 6 samples to correct instrumental deviation. The metabolomics strategy consisted of three different steps: a component detection from MS data using PARADISe [3], a multivariate analysis using EZ-Info and the creation of the statistical models with combinations of responses for compounds with the greatest impact on oil characteristics. Our results, have revealed a great potential for the discrimination of adulterated olive oils, as well as for olive oil classification according to their quality when using metabolomic-based approaches. The full MS spectrum acquisition has allowed the detection and identification of volatile organic compounds (VOCs), responsible of defects in olive oil samples and characteristic of other vegetable oils in case of adulteration in a very short analysis time (5 minutes). The developed procedure applied to 120 olive oil samples allowed to tentatively identify compounds responsible for defect and inherent to different vegetable oils, as well as to create a classification methodology. This classification method was finally validated using blind samples, obtaining an accuracy in oil classification of 80 % taking the official established method, "PANEL TEST" as reference, with a 100% of lampante samples correctly classified. Adulteration of olive oil with different vegetable oils was able to be detected in a 5 minutes run, at concentrations of vegetable oils lower than 5%.

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P-OT-02

UNTARGETED MULTI-PLATFORM METABOLOMICS APPROACH FOR THE STUDY OF CHILDHOOD CEREBELLAR ATAXIA

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Ataxia in children is a common clinical sign of various origins consisting of impaired coordination of movement and balance with a lack of muscle control during voluntary activity [1, 2]. Ataxia is most frequently caused by dysfunction of the complex circuitry connecting the basal ganglia, cerebellum and cerebral cortex, and this type of involvement is recorded as “cerebellar ataxia”. In this research we investigate the metabolic profile of several patients with cerebellar ataxia. The study included plasma samples and urine samples from 10 kids, 5 of them affected by cerebellar ataxia (AA) and 5 healthy control (HC). The objective of the work is to find metabolomic patterns that can be associated to the disease. The samples were analyzed by a multiplatform approach [3, 4] using liquid chromatography, gas chromatography and capillary electrophoresis coupled to mass spectrometry. The LC (Agilent 1200)-QTOF-MS (Agilent 6520) experiments were performed for plasma and urine samples in positive and negative ionization modes. LC-MS/MS fragmentation experiments were also performed for structure elucidation of the analytes of interest. For the GC (Agilent 7980A)EI-Q-MS (Agilent 5975C) experiments, plasma samples were derivatized and analyzed according to the Fiehn method [5]. Urine and plasma samples were analyzed in positive mode for the CE (Agilent 7100)-TOF (Agilent 6224) analyses. Despite the low number of samples, the data showed interesting results. After multivariate and univariate statistical analysis, 52 significant chemical signals were found to differentiate AA and HC children in the plasma samples. Similarly, 10 compounds were found to significantly differentiate between AA and HC in the urine samples. Most of the compounds found in plasma belonged to the groups of fatty acids, bile acids, aminoacids, sugars, carnitines and small organic acids. The compounds found in urine were mainly aminoacids derivatives and sugars and derivatives. A trend of increased levels of different types of carnitines, fatty acids and small organic acids was found in all AA subjects. Some sugars were found to be decreased as well as some aminoacids.

This preliminary study could contribute to understanding biochemical changes associated to the disease and even proposing potential diagnostic markers for ataxia, but further research has to be carried to validate current results.

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P-OT-03

EVALUATION OF MASS SPECTRAL FINGERPRINTS BY SPME FOLLOWED BY MS FOR CHARACTERIZATION OF HONEY BOTANICAL SOURCE

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Honey aroma, which depends on its volatile composition, is one of its most appreciated properties and a subject of great interest in apiculture, as it often determines honey selection by consumer. The wide number of honeys from different botanical source (unifloral, multifloral and honeydew honeys) marketed nowadays makes difficult their characterization for authentication purposes, or to increase their added value in the case of honeys with protected designation of origin. In this sense, the development of fast, reproducible and non-biased methodologies based on Direct Injection Mass Spectrometry could be an approach worthy of evaluation.

Whereas methodologies based on Solid Phase Microextraction (SPME) followed by/coupled to Gas Chromatography-Mass Spectrometry (GC-MS) have been previously reported for authentication of honey botanical origin [1,2], as far as we know, only a previous reference [3] has addressed the botanical discrimination and classification of honey samples based on mass spectral fingerprints collected by SPME.

In this work, 24 commercial honeys of 5 different botanical sources (citrus, eucalyptus, rosemary, acacia and honeydew honey) were analyzed [1] using two different SPME fiber coatings (Polyacrylate and Carboxen/Polydimethylsiloxane). In a simulation of a non-separative approach, combined mass spectra from GC-MS profiles were used as mass spectral fingerprints for each of the honey samples under analysis. After corresponding data pretreatment (removal of artifacts or background noise signals) and normalization, the set of combined mass spectra previously obtained were subjected to different supervised and unsupervised pattern recognition techniques. The most significant mass to charge ratios (*m/z*) for classification of honey botanical source were determined and compared among the different multivariate statistical analysis techniques here evaluated. Potential markers were identified from selected *m/z* ratios and from GC retention data.

As conclusion, mass spectral fingerprints obtained by SPME followed by MS seem to be a promising alternative to conventional GC-MS approaches for authentication of honey botanical source.

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P-OT-04

A HUMAN DIETARY INTERVENTION STUDY OF A BIOACTIVE GARLIC SUPPLEMENT BY A FINGERPRINTING METABOLIC APPROACH

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Garlic (Allium sativum) has been of great interest since ancient times because of its healthy properties which prevent and improve certain diseases [1,2]. With the aim of knowing the changes in the human plasma-metabolome due to the ingestion of a bioactive garlic food supplement, a dietary intervention assay was performed in 30 healthy people. Plasma samples were collected before starting intake and after consuming the garlic supplement for one month. These samples were properly treated and analysed by HPLC-ESI-QTOF-MS. Subsequently, after data processing (Molecular Feature Extraction, Normalization…) and the corresponding univariate (paired t-test and paired fold change) and multivariate statistical tests (PCA, PLS-DA, HCA), a total of 39 features were obtained as statistically significant due to supplement intake. 26 metabolites of them could be tentatively identified and in general, alterations in phospholipid metabolism were detected because of the plasma concentration increase of mainly lysophosphatidylcholines, lysophospatidylehanolamines and several acylcarnitines. The most distinguished result was the great number of significant lysophosphatidylcholines whose concentrations increased after the supplementation. On the other hand, it is also remarkable that the concentrations of four fructosamines decreased after the assay. Both results are according with the antioxidant and antiglycation properties that have been previously associated with garlic extracts.

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P-OT-05

A MULTI-PLATFORM METABOLOMIC APPROACH TO SEARCH CHEMICAL MARKERS RELATED TO THE COFFEE ROASTING PROCESS

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Coffee is one of the most consumed beverages in the world due to its excellent organoleptic and stimulant properties. Among the different coffee varieties, *Arabica* coffee is the most consumed since it has higher sensory properties than other species. One of the most critical steps in coffee processing is roasting. During this process, green coffee beans suffer many changes in their chemical and physical composition that affect the quality of this beverage. For this reason, it is important to have a tool to control and characterize the roasting process. Metabolomics is a powerful tool capable of providing an exhaustive characterization of coffee samples submitted to different roasting degrees and allowing the search of chemical markers characteristics of each roasting degree. However, the number of works concerning the non-targeted metabolomic study of coffee roasting process is scarce.

The aim of this work was to develop three different non-targeted metabolomic platforms based on the use of reversed-phase liquid chromatography (RPLC), hydrophilic interaction chromatography (HILIC) and capillary electrophoresis (CE) coupled to high resolution mass spectrometry (QTOF) to characterize *Arabica* green coffee beans submitted to three different roasting processes (light, medium, and dark). Non-supervised and supervised multivariate analyses were performed to point out the most significant markers allowing, in all cases, a good sample discrimination. Those variables having a high variable importance on projection values on supervised analysis were selected as significant metabolites for the identification and further interpretation. Interestingly, the results showed that the metabolites can follow two different trends; some gradually changed over roasting process whereas others were characteristic only from a specific roasting degree. The results obtained for the three proposed approaches were complementary. Thus, the potential markers found in this study were hydroxycinnamic acids and flavonoids in RPLC-MS, betaines and amino acids in HILIC-MS and amino acid derivatives and metabolites related to the Maillard reaction in CE-MS. This is the first time that a multiplatform metabolomic approach has been developed to evaluate changes in coffee profile over roasting process.

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P-OT-06

MULTI LC-MS METHOD APPROACH FOR THE VALIDATION OF POTENTIAL BIOMARKERS FOR THE EARLY DIAGNOSIS OF PARKINSON'S DISEASE

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Parkinson's disease (PD) is a complex and progressive neurodegenerative disease mostly characterized by impairments in motor systems due to degradation of dopaminergic neurons [1]. Other symptoms such as cognitive impairment, dementia and psychiatric symptoms can also be present in patients with PD. Diagnosis of PD is primarily clinical according to presence of typical symptoms. Therefore, biomarkers that may provide earlier diagnosis of PD, even before its development, may increase efficiency in treatment and identification of potential risk groups [2].

The aim of this work was to develop and validate analytical methods that will allow to find potential biomarkers for the early diagnosis of this disease. The work enrolled plasma samples as part of "The European Prospective Investigation into Cancer and Nutrition" study (EPIC)-Spain study. Plasma samples were collected from healthy donors, who were followed up for 15 years. Therefore, these plasma samples are of great value for the discovery of biomarkers for the early diagnosis of PD and other diseases and makes this study a high risk project involving the validation of biomarkers in healthy subjects. Some of the donors that developed PD after the sample collection are included in the present work (n=12), as well as healthy controls (n=21) from the same prospective study.

The 56 analytes chosen for this target work are selected according the previous works on PD, in which variations in the concentration of certain metabolites are related to the disease [3-5]. Two different systems were used for it (Agilent 6460 QQQ LC-MS and Agilent 6470 QQQ LC-MS). Four methods were developed for the determination of different sets of analytes according to their suitability, as well as for the sample analysis and quantitation. The first method made use of ion-pairing with tributylamine for the separation of polar compounds in RPLC [6]. A RPLC column with high carbon load was selected for the second and third methods, using different mobiles phases.

The fourth method made use of a HILIC column for the separation of some particular small polar compounds. All the methods have been validated in terms of repeatability, intermediate precision, accuracy/recovery, linearity, limit of quantitation and stability.

The obtained results showed good repeatability (0.3-9.3 % RSD) and intermediate precision (3.1-27.7 % RSD) for the analyzed compounds. The limit of quantitation for the most of the analytes was below 200 ppb, while the linearity mostly showed a wide range between 1 ppb and 1 ppm. Most of the compounds also showed good recoveries and good stability over 72 h, in the sample matrix as well as in pure standard solutions, at room temperature and at 4 ºC. The proposed multi LC-MS approach has been proven to be useful for the study of the proposed metabolites and represents the starting point for the future validation of a set of biomarkers for the early diagnosis of PD within EPIC-Spain.

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P-OT-07

ANALYSIS OF PROTEIN BIOMARKERS BY ON-LINE IMMUNOAFFINITY SOLID-PHASE EXTRACTION CAPILLARY ELECTROPHORESIS-MASS SPECTROMETRY USING Fab' ANTIBODY FRAGMENTS. TRANSTHYRETIN IN FAP-I.

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The analysis of low abundant proteins in biological fluids by capillary electrophoresis (CE) is particularly problematic due to the typically poor concentration limits of detection of microscale separation techniques [1]. This study describes an on-line immunoaffinity solid-phase extraction capillary electrophoresis mass spectrometry (IA-SPE-CE-MS) method, using an immunoaffinity sorbent with Fab' antibody fragments (Fab'-IA), for the analysis of serum transthyretin (TTR), a homotetrameric protein ($M_r \simeq 56{,}000$) involved in different types of amyloidosis [2].

The IA sorbent was prepared by covalent attachment of Fab' fragments obtained from a polyclonal IgG antibody against TTR to succinimidyl silica particles [3]. The Fab'-IA-SPE-CE-MS methodology was first established analyzing TTR standard solutions. Under optimized conditions, repeatability and reproducibility were acceptable, limits of detection (LODs) were around 0.5 $\mu g \cdot mL^{-1}$ (50-fold lower than by CE-MS) and different TTR conformations were observed (folded and unfolded). The applicability of the developed method to screen for familial amyloidotic polyneuropathy type I (FAP-I), which is the most common hereditary systemic amyloidosis [2], was evaluated analyzing serum samples from healthy controls and FAP-I patients. For the analysis of sera, the most abundant proteins were precipitated with 5% (v/v) of phenol before Fab'-IA-SPE-CE-MS.

The current method enhanced our previous results for the analysis of TTR using intact antibodies immobilized on magnetic beads [4]. It allowed a slight improvement on LODs (2-fold), the detection of proteoforms found at lower concentrations and the preparation of microcartridges with extended durability. Furthermore, results with TTR could be regarded as a starting point for the analysis of other small or large biomarkers by Fab'-IA-SPE-CE-MS.

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P-OT-08

METABOLOMICS FINGERPRINTING OF BILE SAMPLES IN A CHOLANGIOCARCINOMA STUDY

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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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P-OT-09

UNVEILING THE CAPABILITIES OF CE-LIF FOR DETERMINATION OF KEY FREE D-AMINO ACIDS IN HUMAN URINE. APPLICATION TO THE STUDY OF THEIR RELATIONSHIP WITH FERMENTED DAIRY FOOD INTAKE

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Most AAs of importance in nutrition exist as L-isomers. Natural proteins in humans are exclusively built from L-AAs whereas D-AAs found in biological specimens are originated from (1) daily foods and drinks (mainly fermented foods), (2) bacterial metabolism in the gut or de novo synthesis. In mammals, among other mechanisms, conversion by the oxidases in kidney is proposed as the main regulator of the levels of D-AAs even though is species dependent. It is noteworthy that the several practices for processing food can induce the racemization of L-AAs to D-AAs.

The presence of D-AAs in biological samples from humans is mainly attributed to diet and to the metabolism of intestinal bacteria. Quantitation of D-amino acids has become a hot topic in bioanalysis nowadays and the influence of food intake is mostly unknown.

Capillary electrophoresis coupled to fluorescence detection CE-LIF offers high efficiency and sensitivity, especially in the analysis of AAs in biofluids. As D-amino acids clearance takes place mostly as renal excretion, urine samples may constitute a good basis for its determination. Due to the poor or absent fluorescence of natural amino acids, it is necessary to include a rapid and efficient labeling agent suitable for the Argon ion laser source, such as 4-fluoro-7-nitro-2,1,3-benzoxadiole (NBD-F). In this research different conditions will be tested with this labelling agent and chiral selectors based on our previous experience (1), for improving the separation capability of the method. The best results will be provided for the separation of Gly and 14 pairs of chiral amino acids: L/D-alanine, L/D-aspartate, L/D-glutamate, L/D-glutamine, L/D-isoleucine, L/D-leucine, L/D-lysine, L/D-methionine, L/D-ornithine, L/D-phenylalanine, L/D-proline, L/D-serine, L/D-threonine and L/D-valine. Special conditions will be shown for improving the sensitivity for D-Ser, D-Glu and D-Asp. The final method for the determination of key D-AAs was validated for five D-AAs and applied to the analysis of urine samples from 30 voluntaries: 15 controls and 15 individuals whose dinner consisted only on fermented dairy products. The obtained % D-AA as D/(D+L) were compared to find differences between these two groups and besides, they were compared with values obtained by GC-MS (2). All results will be presented. A simple and rapid method for determination of several free D-AAs ratio in urine is described. It can contribute in further studies for unveiling the influence of D-AAs in health.

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P-OT-10

STUDY OF THE MINOR FRACTION OF VIRGIN OLIVE OIL BY A MULTI-CLASS GC-MS APPROACH: COMPREHENSIVE QUANTITATIVE CHARACTERIZATION AND VARIETAL DISCRIMINATION POTENTIAL

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Virgin olive oil (VOO) minor fraction comprises a heterogeneous mix of molecules, including phenolic compounds (simple phenols, phenolic acids, secoiridoids, flavonoids and lignans), triterpenic compounds (acids and dialcohols), tocopherols and sterols. The determination of these compounds is of undeniable importance to both VOO producers and regulatory bodies, who are continuously challenging the analytical community to offer rapid and accurate testing methods. Multi-class methodologies, which exhibit the ability to monitor analytes belonging to diverse chemical classes in one single analysis, bring out a remarkable progression of the traditional single-class methods in terms of throughput and cost. At the same time, they enlarge the information achievable by the analyst and provide enhanced possibilities to take advantage of the results.

For the first time, a multi-class GC-MS method was applied to identify and quantify more than 40 compounds from the VOO minor fraction in a single run. This innovative methodology has demonstrated a comprehensive profiling ability on, at least, five groups of compounds with wide range of polarities/volatilities and chemical entities [1]. First, highly satisfactory results were achieved regarding linearity, sensitivity, accuracy and matrix effect during method validation. Second, 32 VOO samples from eight different cultivars (some of them very scarcely studied before) were analyzed by applying the proposed methodology and the quantitative results were subjected to chemometrics. Both non-supervised and supervised multivariate statistical tools were used for testing the capability of the determined VOO minor compounds to discriminate the varietal origin of the samples, pointing out potential chemical markers of each cultivar.

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P-OT-11

EXPLORING THE CAPABILITY OF LC-MS AND GC-MS MULTI-CLASS METHODS TO DISCRIMINATE OLIVE OILS FROM DIFFERENT GEOGRAPHICAL INDICATIONS AND TO IDENTIFY POTENTIAL ORIGIN MARKERS

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Protected Designations of Origin (PDOs) and Protected Geographical Indications (PGIs) are important tools to promote high quality extra virgin olive oils (EVOOs), assuring the connection to a particular territory and the unique combination of natural and human factors which make possible to obtain matchless oils. For that reason, it is imperative to furnish the control labs with innovative tools and methods which are able to provide extensive information about the minor fraction of an oil (of unquestionable importance regarding its overall quality) and to give the chance to find, identify (and validate) origin markers.

In this contribution, 126 EVOO samples from six different Mediterranean GIs (Priego de Córdoba and Baena (Spain), Kalamata (Greece), Toscano (Italy), and Ouazzane and Meknès (Morocco)) were analyzed by means of two different platforms (LC-ESI-QTOF MS (in positive and negative polarity) and GC-APCI-QTOF MS (in positive mode)) combined to chemometrics. The sample treatment and chromatographic/detection conditions (in both platforms) were chosen to enable the comprehensive characterization of the complete minor fraction of the oils within a single run. The capabilities of the software used for the data treatment (MetaboScape) gave us the chance to build statistical models (two-class PLS-DA models) to discriminate among the selected samples pointing at potential classifiers (which were identified to a great extent, thanks to the annotation tools included within the software package and the use of specific standard mixtures, isolated VOO fractions and representative oil blends). The different polarities and platforms logically drove to diverse makers, taking advantage of their complementarity and, consequently, enriching the outcomes of the project. The definition of distinct compositional patterns of each GI was a very valuable accomplishment.

The utility of validated classifiers to authenticate the belonging (or not) of an EVOO to a particular GI is not open to debate. The consumers' confidence will be perceptibly undermined if the geographical name is used on products not having the expected qualities or if the production specifications are sometimes not followed by producers.

P-OT-12

LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY ANALYSIS OF EICOSANOIDS

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Eicosanoids, including prostaglandins and leukotrienes, are biologically active lipids that have been implicated in various pathological processes, such as inflammation and cancer. We have developed an ultra-performance liquid chromatography–multiple reaction monitoring/mass spectrometry (UPLC–MRM/MS)-based, that enables simultaneous profiling of multiple lipids produced ex vivo in human plasma. We employed a triple–quadrupole mass spectrometer coupled to a UPLC system, to measure absolute amounts of 10 distinct eicosanoids. In a 15.5-min run, we resolved and detected with high sensitivity all targeted analytes from a very small plasma sample (5 µl). We conclude that liquid chromatography-tandem mass spectrometry methodology is a versatile and reliable analytical tool for the simultaneous analysis of the eicosanoids in human plasma samples at concentrations on the nM threshold.

P-OT-13

NEW POTENTIAL BIOMARKERS OF METASTATIC COLORECTAL CANCER USING AN UNTARGETED LC-HRMS-BASED METABOLOMICS

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Colorectal cancer (CRC) is one of the main causes of cancer death worldwide, although early detection and diagnosis makes cure more feasible. Searching for new diagnostic biomarkers seems vital to improving the survival rate of these patients. Metabolomics, a powerful tool focused on the presence and/or concentration of low-molecular weight in different body fluids, is aimed at constructing a fingerprint that is unique to each individual and pathological state. The purpose of our study was to identify a differential metabolomic signature for metastatic colorectal cancer using serum samples from 125 individuals: 60 healthy controls and 65 metastatic colorectal cancer patients. Samples were analyzed using reverse phase liquid chromatography coupled to high-resolution mass spectrometry in the electrospray positive ionization mode. Multivariate statistical analysis revealed a clear separation between both groups. The receiver operator characteristic (ROC) curves analysis was applied to explore the changes in concentrations of endogenous metabolites potentially involved in metastatic CRC. Based on this, different levels of endocannabinoids, glycerophospholipids and sphingolipids were found in the serum from patients compared to controls, so we suggest that liquid chromatography-high resolution mass spectrometry-based metabolomics is a potent diagnostic tool for metastatic colorectal cancer.

P-OT-14

INFLIXIMAB AND CETUXIMAB-THERAPEUTIC MONOCLONAL ANTIBODIES-N-GLYCOSILATION ANALYSIS BY UPLC-FLUORESCENCE-QTOF (MS)

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Infliximab (Remicade, Janssen Biologics B.V.) is a chimeric human-murine monoclonal antibody IgG1 directed against tumour necrosis factor alpha (TNFα), manufactured from a recombinant cell line. [1]. Cetuximab (Erbitux, Roche Pharma AG) is also a chimeric monoclonal IgG1 antibody produced in a mammalian cell line (Sp2/0) by recombinant DNA technology. It is directed against the human epidermal growth factor receptor (EGFR) [2].

The efficacy of these therapeutic proteins is highly dependent on the correct glycosylation patterns. As human IgG, they have a single conserved N-linked glycosylation site located on the Fc region of each heavy chain at the amino acid residue Asn-297. Therefore, each unit has two sugar chains (glycans), which are characterized by a high heterogeneity which means that it can contain different glycan types up to 30 [3]. Then, this inherent heterogeneity of should be controlled.

Labeled N-glycans were separated in a hydrophilic interaction chromatographic (HILIC) column using an ultra performance liquid chromatograph with sequential fluorescence and accurate mass quadrupole time of flight (QToF) mass spectrometric detection with an electrospray ionization interface (Waters Corporation Milford, MA, USA). Mass spectrometric data collection and processing was controlled using MassLynx 4.1 (Waters Corporation, Milford, MA, USA). Previous to the analysis, infliximab samples were treated to perform glycan release by enzymatic digestion (PGNase F) and labeling for subsequent fluorescent detection using 2-aminobenzamide (2AB).

The particular fluorescence glycan profiles of infliximab and cetuximab were obtained and, as expected, they were different and characteristic of each one. A tentative assignation of the glycans from the mass spectrometric data was performed. These results contribute to a full characterization of these important therapeutic proteins and also to be compared with other results obtained on different batches of these drugs in order to evaluate heterogeneity due to the glycans profiles.

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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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P-OA-02

CHALLENGES IN THE ANALYSIS OF SYNTHETIC DYES IN COSMETICS BY REVERSED PHASE LIQUID CHROMATOGRAPHY COUPLED TO TANDEM MASS SPECTROMETRY

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Synthetic dyes are added to cosmetic preparations in order to colour the cosmetic itself and/or the body as a whole or certain parts thereof, by absorption or reflection of visible light. They are widely used in personal care products in spite of many studies confirming their negative influence on human organism. As pointed out in a recent revision on analytical methodologies [1], the majority of the studies for the determination of dyes are focused on food samples meanwhile there are only a few methods published in the international literature for their analysis in cosmetics. Due to the hydrophilic nature of dyes, liquid chromatography is the most usual choice in combination with absorbance detectors, and more recently with mass spectrometry due to its enhanced sensitivity and selectivity. Most of synthetic dyes are sodium or calcium salts that contain in their structures one or more ionized groups such as sulphonic groups. Separation of ionic compounds by reversed phase liquid chromatography requires more efforts compared to the separation of neutral compounds [2].

The aim of this work is to present the optimization of the parameters influencing the chromatographic separation of ionized and neutral dyes [3-5]. Analysis was carried out by LC-MS/MS for a broad range of dyes with different chemical structures. Factors affecting the mobile phase (ionic strength, pH, and composition) were investigated and two stationary phases (porous and core-shell) were employed. Moreover, matrix effects as well as method quality parameters were studied for all the optimized methods.

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P-OA-03

STUDY OF PHOTODEGRADATION OF PATENT BLUE V IN ORAL CARE PRODUCTS

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To guarantee the safety of daily-use products, particularly those that are exposed to light in transparent bottles for long periods such as mouthwashes, photochemical behaviour of their ingredients must be investigated.

Some studies about the photochemical stability of a few synthetic dyes mainly in soft drinks [1, 2] have evidenced a strong relation between the matrix composition and the photoproducts formed. Some of the chemical structures proposed for the photoproducts identified are based on aromatic amines, which suggest a potential hazard for consumer health. Despite of these results obtained in soft drinks, there are not precedents in the international scientific literature about photodegradation of synthetic dyes in cosmetics.

The aim of this work is to investigate the photochemical behaviour of a synthetic dye triarylmethane, Patent Blue V, in aqueous solution and in oral care products. In order to assure a continuous availability and constant intensity of irradiation, Suntest CPS+ was employed to irradiate the samples. A xenon lamp (from 800 to 300 nm) and different filters simulating outdoor and indoor conditions were used. To evaluate the kinetics of degradation, aliquots of sample were taken and their absorbance was measured by UV-Vis spectrophotometry. Factors affecting the photostability of the dye such as matrix composition, pH, or the presence of oxygen, were studied in various commercial oral care formulations.

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P-OA-04

EVALUATION OF THE EFFECT OF AIR-DRYING TEMPERATURE ON PHENOLIC COMPOUNDS OF AVOCADO BY-PRODUCTS BY HPLC-ESI-TOF-MS

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Avocado (*Persea americana* Mill., Lauraceae) is an important oleaginous fruit, source of bioactive compounds with healthy benefits. Industrially, only the avocado pulp is exploited as guacamole or other products generating a large quantity of seed and peel, which are discarded with no further applications. These by-products represent around 30 % of the total weight of the fresh fruit, so its waste could cause environmental problems with high cost for the food processing industry. Besides, the avocado seed and peel had high amounts of extractable bioactive compounds, as polyphenols, which could be used in many applications due to their well-known bioactivity. Nevertheless, one of the main challenges involved in the use of avocado by-products is their high water activity. Therefore, drying is an essential step in the revalorization of these industrial by-products in order to decrease the water content to a level at which microbial spoilage and deterioration reactions are minimized. In this sense, the effect of air drying temperature on total polyphenol content (TPC) and individual phenolic compound concentrations presents in avocado peel, seed and seed coat was evaluated. For this purpose, a sensitive HPLC-DAD-ESI-TOF-MS method has been developed. The best results for all the matrices were obtained with the shortest drying process, performed at 85°C. Under this optimal drying temperature the maximum TPC for avocado peel, seed and seed coat were 58 ± 4, 29.5 ± 0.4 and 71 ± 2 mg EAG/g dm, respectively. Respect to individual concentrations, more than forty phenolic compounds were simultaneously quantified by HPLC-DAD-ESI-TOF-MS to assess the effect of drying temperature on individual compounds. Nevertheless, different optimum drying temperatures were obtained for the evaluated individual compounds. In general, phenolic acids were the most stable compounds during the drying process regardless of the applied temperature. On the opposite, procyanidins suffered an important degradation with longer drying steps. Furthermore, the results showed that the type A procyanidins were more thermostable than type B, and the degradation increased with the polymerization degree. It can be concluded that the optimized drying process performed at 85°C in a forced air oven seems to be a suitable process for industrial scale in order to dry the avocado peel, seed and seed coat by-products before its transport or processing with minimum losses of phytochemicals. To our knowledge, this is the first available study in which such amount of phenolic compounds was quantified in avocado by-products.

P-OA-05

PREPARATION OF A O-[2-(METHACRYLOYLOXY)-ETHYLCARBAMOYL]-10,11-DIHYDROQUINIDINE-SILICA HYBRID MONOLITH FOR THE ENANTIOSEPARATION OF AMINO ACIDS BY NANO-LC

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Organic hybrid monolithic columns have been developed because of their excellent permeability, more pH stability, high surface and high performance [1]. Compared to the polymer-based and silica-based monoliths, organic hybrid monoliths present some advantages such as the less shrinkage and easy preparation that have attracted more and more attention [2]. So far, quinidine functionalized monoliths can be divided into silica-based and polymer-based, and quinidine functionalized organic hybrid monolithic columns have never been described. Just two functionalized organic hybrid monoliths based on the structurally similar quinine have been reported [3,4]. Thus, Tran *et al.* developed quinine-silica/zirconia and *tert*-butylcarbamoylquinine-silica hybrid monoliths. However, the preparation process was time-consuming due to the multi-step temperature regulation. In this work, an O-[2-(methacryloyloxy)-ethylcarbamoyl]-10,11-dihydroquinidine (MQD)-silica hybrid monolithic column was prepared by a facile "one-step" strategy within a 100 µm I.D. capillary. The influence of methanol, ethylene glycol, and water contents, tetramethoxysilane and vinyltrimethoxysilane volume ratio, reaction temperature, and cetyltrimethylammonium bromide and MQD monomers contents, was investigated to obtain a satisfactory morphology for the monolithic columns. The optimized MQD-silica hybrid monolithic columns exhibited good permeability, stability, efficiency and reproducibility. Reversed phase mode and polar organic phase mode conditions were systematically optimized for *N*-derivatized amino acid analysis in nano-LC. A total of 52 protein and non-protein *N*-derivatized amino acids were enantioresolved using the synthesized monolithic column.

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P-OA-06

BREATH ANALYSIS FOR THE BIOLOGICAL MONITORING OF CHRONIC EXPOSURE TO VOLATILE ORGANIC COMPOUNDS

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Conventional occupational exposure studies are based on the analysis of workplace air samples and the determination of limit levels in air that could lead to acute effects. However, simply monitoring air levels alone may not be sufficient to evaluate exposure in chronic conditions. Biological monitoring assesses the health risk through the evaluation of the internal dose and determines the amount of a chemical agent or its metabolites in a biological fluid. It is considered a reliable exposure assessment methodology because integrates exposure from all routes [1]. Urine and blood are the most common fluids evaluated in biological monitoring but breath has demonstrated to be a promising alternative for biological monitoring [2].

An "in-house" capillary thermal desorption (cTD) device connected to a GC-MS was previously developed in order to reach the low levels expected in non-occupational exposure conditions (pptv or $\mu g \cdot m^{-3}$) and using small volumes of breath samples (<1 L). This cTD allows reaching method detection limits in the 5-15 pptv range (i.e., 15-50 $ng \cdot m^{-3}$) with only 0.75 L of samples being required [3]. Breath samples from 216 volunteers in three different non-acute exposure conditions have been evaluated: (i) exposure to sevoflurane and isopropyl alcohol in hospital environments (n=100), (ii) exposure to solvents in research chemistry laboratories (n=86), and (iii) passive smokers (n=30).

In all the situations evaluated, conventional exposure analyses through the assessment of air levels indicated that the evaluated environments cannot be considered as harmful from an occupational point of view. However, the use of breath analysis for biological monitoring confirmed a clear and significant accumulation of the target contaminants in all people being in environments considered as non-polluted and safe, which could have chronic effects in situations of continuous exposure to these environments. In the case of research laboratories, some solvents were detected well above the recommended inhalation reference concentration (RfC) values estimated by the US-EPA, which are levels associated to chronic effects for continuous inhalation exposure.

The results obtained indicate that breath analysis presents multiple advantages for biological monitoring as it is neither invasive nor embarrassing for people, and is simpler and faster than conventional biomonitoring methods based on urine or blood analysis.

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P-OA-07

PHYTOCHEMICAL PROFILING OF HYDROALCOHOLIC EXTRACT FROM AERIAL PARTS AND ROOTS OF *RUTA GRAVEOLENS* FROM MORELOS (MEXICO)

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Ruta graveolens, commonly known as rue, is an herbaceous perennial plant with bluish-green leaves that emits a powerful odor and have a bitter taste. This species is original from the Mediterranean region and has been cultivated in several countries all around the world. This plant has shown different pharmacological activities and is employed in folk medicine for treatment of rheumatism, dermatitis, pain and many inflammatory diseases [1]. The main components reported in *Ruta graveolens* are quinoline, furoquinoline, acridone alkaloids, flavonoids, and coumarins, mainly furanocoumarins [2]. Furanocoumarins have been detected in different parts of the plant (i.e. leaves, stems and roots) [3], whereas acridone alkaloids have been identified in roots and furoquinoline alkaloids were mainly reported in leaves [4]. Since several works in literature report the tissue-specific accumulation of phytochemicals in *Ruta graveolens*, in this work, a comparative phytochemical profiling of metabolites from the aerial part and the root was proposed to verify the distribution of metabolites in the Mexican variety. For the isolation of target metabolites, aerial part and roots were separated, washed, dehydrated at room temperature and submitted to an ultrasound-assisted extraction procedure using ethanol and water mixtures (85:15 v/v) as solvents. The obtained extracts were analyzed and characterized by GC-MS. A similar number of metabolites were identified in both parts of the plant. Acridone and furoquinoline alkaloids, furanocoumarins, terpenes and ketones, were found in both extracts, although at different concentration levels. Roots extracts showed the highest number of alkaloids and furanocoumarins, and the metabolites most abundant were dictammnine, rutacridona and isomaturnina; whereas terpenes and ketones were mainly abundant in aerial part extracts, where the principal metabolites were kokusaginine, arborinine, bergapten, isomartunine and circimaritin. In this work, acridone alkaloid arborinine was only identified in the aerial part, whereas furanocoumarins as isopimpinellin and kokusaginin were exclusively detected in the roots, which reveal that this variety exhibit a different distribution of metabolites from the reported in literature. Arborinine has been reported anticancer activity [5].

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P-OA-08

PYROLYSIS-COMPOUND-SPECIFIC ISOTOPE ANALYSIS (PY-CSIA δ^2H) OF EXTRA VIRGIN OLIVE OILS FROM THE MEDITERRANEAN BASIN

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Stable isotope composition of light bio-elements in plant tissues reflects geo-climatic conditions of the production area, certain local agricultural practices and water uptake [1]. Therefore, the isotope composition of plant-derived fatty acids i.e. of extra virgin olive oil (EVOO), retains this information and its study allows assess both, the origin as well as certain aspects of its production means [2]. Actually, only one study has focused in hydrogen/deuterium (δ^2H) isotope ratio composition of specific fatty acids in EVOO samples [3]. Analytical pyrolysis (Py-GC) when combined with isotope ratio mass spectrometry (IRMS) (Py-CSIA) allows the simultaneous analysis of different specific compounds in the same analysis minimizing sample manipulation [4]. Here, Py-CSIA is used as tool for tracing the correlation between geographic variables and the hydrogen compound-specific isotope composition of EVOOs produced in the Mediterranean Basin.

A total of 6 EVOO samples from 5 different Mediterranean countries (Portugal, France, Tunisia, Turkey and Spain) were sampled. Each sample was geo-referenced, obtaining data of altitude (m.s.a.l), oceanic distance (km), longitude (UTM), latitude (UTM), mean annual precipitation (mm) and mean annual temperature (^{o}C). The hydrogen compound-specific isotopic composition (δ^2H) of EVOOs was obtained by analytical pyrolysis (Py-CSIA) at 400 ºC (1 min).

The δ^2H value of the 11 major pyrolysis compounds present in all EVOO samples ranged between -120 and -270 mUr. Three representative major pyrolysis peaks of EVOO: palmitic acid, oleic acid and squalene, were selected as possible markers surrogated to the oil geographic origin. After a principal component analysis (PCA), it was found that δ^2H was highly correlated with the geographic longitude of the production area. A partial least square (PLS) regression analysis indicated that using the δ^2H value of the 3 major pyrolysis compounds it was possible to predict ($P<0.05$) altitude, oceanic distance and geographical longitude of EVOO production site. Although a wider study is necessary (in course) to include more locations and conditions, the results described here suggest that this methodology is of high potential to assess geographic origin and even growing conditions of EVOOs and to detect fraud activities.

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P-OA-09

DETERMINATION OF LIMONENE IN RECYCLED HDPE PELLETS

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A simple and efficient solvent extraction method with gas chromatography and mass spectrometry for the determination of the odorant Limonene in recycled high-density polyethylene plastic (HDPE) pellets to provide assurance the levels of Limonene do not exceed the maximum permitted concentration and thereby qualifying the use of recycled HDPE pellets to be used in food packaging.

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P-FA-01

ANALYSIS OF PESTICIDES IN TEA LEAF AND HONEY USING THE NEW INTUVO PLATFORM COUPLED TO GC MS/MS

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As pesticide use has increased, so has the level of concern among environmentalists, regulators, and consumers. Growing demand has increased the use of pesticides and expanded poor agricultural practices, elevating risks in the food supply and the environment. Regulating bodies around the globe have established regulations regarding the maximum residue levels (MRLs) of pesticide that can be found in or on food.

The complexity of pesticide analysis, the low quantitation limits, and MRL ranges drive the need for a multiresidue quantification method with a reasonable linear range and low limits of detection.

For this reason, tandem mass spectrometry (MS/MS) is used for screening, confirming, and quantifying low-level pesticides. It not only provides low limits of quantitation, but also allows for higher selectivity to minimize matrix interferences.

This poster presents the results of the evaluation of multiresidue pesticide analysis for loose-leaf black tea and organic honey on the Agilent Intuvo 9000 gas chromatograph (GC) and an Agilent 7000C triple quadrupole gas chromatography/mass spectrometry (GC/MS) system. Calibration curves for targeted pesticides showed excellent linearity (97% of compounds maintained a $R^2 \geq 0.990$) for concentrations ranging from 5 to 500 ppb. For all compounds analyzed in honey, the limits of quantitation (LOQs) were found to be below 7 ppb where MRLs are between 10 to 50 ppb. For 94% of the compounds analyzed in tea, the LOQs were found to be below 100 ppb where MRLs are between 20 to 200 ppb. All analyzed pesticides obtained a %RSD of repeated measurements of ≤30 % with recovery errors under 30 %.

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P-FA-02

ANALYSIS OF HALOANISOLES AND TRIOCTENON IN WINE USING SPME COUPLED GAS CHROMATOGRAPHY AND TIME-OF-FLIGHT MASS SPECTROMETER

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Trace levels of some compounds can modify organoleptic properties in wine. Some of these compounds are well known in the industry and are capable to determine defined odours or flavours, so that TCA (2,4,6-Trichloroanisole) is responsible of cork taint whereas Trioctenon is responsible of truffle taint. The first one is considered as an enemy in terms of wine quality, but the second one is very valued.

As their effect is appreciable in very low concentration levels, SPME was chosen as concentration technique.

Gas chromatography coupled to Time-of-flight mass spectrometry was used to identify and quantify four haloanisoles (TCA, TeCA, TBA, and PCA). One analytical method with great properties was built by means of combination of high acquisition rate, full range TOF mass spectra and high deconvolution power provided by LECO software, which eliminate matrix interferences.

Another proof of the system capabilities is the Trioctenon isomers determination. Parallel experiments were carried out with and without internal standard (IS). Results showed that in this case there are no significant deviations between both alternatives.

P-FA-03

CHARACTERIZATION AND CLASSIFICATION OF ARABICA AND ROBUSTA COFFEES BY LIQUID CHROMATOGRAPHY, MASS SPECTROMETRY AND CHEMOMETRIC METHODS

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Coffee is today one of the most popular beverages in the world. More than one billion cups are consumed every day, with an annual consumption per capita over 5 kg, on average, in Europe. Intake of coffee is associated with a reduced risk of several diseases, such as type 2 diabetes in healthy individuals, probably due to its antioxidant activity. The proven health benefits of coffee brew plenty justifies the consideration of this infusion as a functional food [1]. Polyphenols can be found among the most remarkable bioactive substances in coffee. In fact, coffee is the major source of chlorogenic acids (polyphenolic family of esters of caffeic, ferulic and *p*-coumaric acids with quinic acid) in the human diet and there is plenty of evidence of their important antioxidant activity. Furthermore, the distribution of polyphenols, and other bioactive compounds, in coffee samples may be attributed to the different coffee varieties (i.e. Arabica, Robusta…) as well as the geographical climate conditions, among other parameters. As a consequence, bioactive compound fingerprinting (via metabolomics profiling) can be used as chemical descriptors to achieve characterization and classification, and to authenticate the production region as an important and remarkable product quality factor.

In the present work, C18 reversed-phase high performance liquid chromatography with UV-detection (HPLC-UV) and ultra-high performance liquid chromatography coupled to high resolution mass spectrometry (UHPLC-HRMS) in an Q-Exactive Orbitrap instrument have been applied to the characterization of Arabica and Robusta coffee samples from different production regions by using chemometric methods. For that purpose, 120 commercially available coffee samples belonging to six groups depending on the variety (Arabica and Robusta) and the growing region (Africa, Asia and South-America) were analyzed after brewing the coffee (espresso machine) and filtration. HPLC-UV chromatographic fingerprints, UHPLC-HRMS polyphenolic fingerprints (obtained by using a user target accurate mass database with TraceFinder™ software) and UHPLC-HRMS metabolomic profiles were considered as a source of potential chemical descriptors to be exploited for the characterization and classification of coffee samples by principal component analysis (PCA) and partial least square discriminant analysis (PLS-DA). Patterns correlated to the coffee varieties, the production regions and the coffee roasted grade were observed.

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P-FA-04

DETERMINATION OF POLYPHENOLS IN PAPRIKA (*CAPSICUM ANNUUM* L.) BY UHPLC-ESI-MS/MS. PROTECTED DESIGNATION OF ORIGIN CLASSIFICATION BY PARTIAL LEAST SQUARES DISCRIMINANT ANALYSIS

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In recent years, diets rich in food of plant origin have gained popularity due to their content of bioactive compounds, such as polyphenols [1]. These compounds are a large family of aromatic secondary metabolites well-known for their health beneficial effects and contributing to sensorial attributes. Paprika is a dried and ground spice with distinctive organoleptic properties, obtained from red pepper. La Vera (Extremadura) and Murcia are the only distinguished Spanish varieties with protected designation of origin (PDO), which increases product value making necessary to properly authenticate them. As known, paprika's polyphenolic content is interesting in terms of nutritional information but also it may be employed as a source of potential chemical descriptors to achieve their classification according to the PDO and region of production [2].

In this work, a UHPLC-ESI-MS/MS (QqQ) method was developed to determine 36 polyphenols in paprika samples. A suitable chromatographic separation with an analysis time below 30 min was obtained by using an Ascentis Express C18 reversed-phase (10 cm × 2.1 mm, 2.7 µm) fused-core column. Moreover, a partial least squares discriminant analysis (PLS-DA) model, using PLS_Toolbox 7.8.2 (Eigenvector Research), was proposed for the authentication of paprika samples.

The developed UHPLC-ESI-MS/MS method showed satisfactory limits of detection (down to 0.01 $\mu g \cdot L^{-1}$), linearity ($R^2 \geq 0.995$), run-to-run and day-to-day precisions (RSD ≤ 20%), and trueness (relative errors below 15%). The polyphenolic content of 111 paprika samples from La Vera and Murcia (Spain) and from Czech Republic was quantified by external calibration. In all samples, at least 13 polyphenols were found. When analysing by PLS-DA, the plot of Scores obtained allowed a successful discrimination in accordance with both PDO and production region. This separation was mostly due to syringaldehyde and homovanillic acid as revealed in the PLS-DA Loadings plots. Moreover, the built PLS-DA model showed satisfactory sensitivity, specificity and error values for each class. A discrimination between Murcia and Czech Republic paprika varieties (hot and sweet) was also achieved.

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P-FA-05

DETERMINANTION OF ETHOXYQUIN AND ITS DIMER IN PEAR SKIN AND SALMON SAMPLES BY LIQUID CHROMATOGRAPHY WITH ELECTROCHEMICAL DETECTION

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Ethoxyquin (EQ) is widely used as a synthetic antioxidant in animal feed, an antiscalding agent in apples and pears and as a color preservative in some spices [1]. Although EQ is a commonly used feed additive, it is not authorized as a food additive in the European Union. The main advantages of EQ are high antioxidant capacity and low production cost. In vitro studies have shown that EQ induces chromosomal aberrations in human lymphocytes [2]. EQ oxidation generates other compounds with antioxidant capacity, namely the major oxidation product the EQ-dimer (EQDM) [3]. The European Union (EU), with the main objective of protecting consumer health, has established a regulation to set the maximum residue limit (MRL) in food samples. EU-MRL is 0.05 mg kg^{-1} for all basic products with exception of pears where the MRL is 3 mg kg^{-1} [4].

Since the presence of EQ in food products could cause negative health effects it is necessary to develop reliable analytical methods to evaluate the risk of human exposure. In this work, a sensitive, selective and accurate method based on solid-liquid extraction followed by clean-up with solid sorbent and liquid chromatography–electrochemical detection analysis with boron doped diamond electrode (LC–EC) for the determination of ethoxyquin and its dimer (EQDM) in pear skin and salmon samples, was developed. The method was validated according to the European Commission guidelines. The main variables of extraction were accurately optimized. The amounts of solid sorbents for clean-up procedure were optimized by using experimental design. A Box-Behnken design to obtain the optimum conditions was applied. For validation, a matrix-matched calibration was established and a recovery assay with spiked samples was carried out. The limits of detection (LODs) found were 0.05 and 0.1 mg kg^{-1} for EQ and its dimer, respectively. The precision (as relative standard deviation, RSD) was lower than 15% with recoveries of compounds close to 100% in spiked samples.

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P-FA-06

DEVELOPMENT AND VALIDATION OF LC-MS/MS METHOD FOR THE CHARACTERIZATION OF REFERENCE MATERIALS FOR PESTICIDES RESIDUES ANALYSIS IN FRUITS: A METROLOGICAL APPROACH

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The state of the art of analytical instruments currently applied to the analysis of contaminants in food has allowed the production of highly accurate data even at low concentration levels, nevertheless it is always necessary to improve and optimize measurement methods to meet high accuracy and lower uncertainty requirements. In the characterization of reference materials, these requirements are much more demanding, inasmuch as the measurement methods are intended for certification, homogeneity assessment and stability studies. For example, the characterization requires minimally biased methods, usually with target uncertainties of at least one third of a typical routine methodology; the homogeneity assessment call upon the best available repeatability and the classical and isochrones stability studies require methods with good precision [1].

In order to development an in-house LC-MS/MS method for multiresidue pesticides for the characterization of reference materials, a metrological approach focused on three key stages of the measurement method was applied. The addressed stages were the extraction, acquisition and quantification steps. For the extraction phase a gravimetric QuEChERS [2] approach was employed, for the instrumental acquisition an electrospray ionization in positive ion mode with multiple reaction monitoring (MRM) was applied, regarding only the quantification ion for each pesticide, taking advantage of metrological point of view where the measurand can be carefully controlled, and finally an one point gravimetric standard addition quantification including the standard uncertainty was used for the quantification stage [3,4]. This approach significantly decrease the method uncertainly and produce a method validated with more stringent acceptance criteria (e.g. respect to the SANTE criteria [5]), which can be used for the characterization of reference materials for proficiency testing.

The validation of the multiresidue method was carried out on 60 pesticide residues in purple passion fruit by LC-MS/MS. The results show that the metrological approach focused on the tree method laps, has a lower uncertainly than others method employees in characterization reference materials[6], it can provide a S/N near to 1000 fold major respect to routine method with a higher precision, the RSD is almost an a half of a routine method (i.e. ≤ 10 % for most pesticides). In addition, the LOQ values were mostly 1 µg kg^{-1} for almost all pesticides, with a mean recovery within the 80–120%.

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P-FA-07

PLASTICIZERS IN CAPSULES OF DIETARY SUPPLEMENTS FOR OVERWEIGHT CONTROL

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Obesity is considered a growing health problem in many developed countries with undebatable and increasing social and economic consequences. Overweight should desirably be controlled through appropriate medical treatment. However, evidences demonstrate an increasing uncontrolled consumption of food supplements for overweight control (FSOC) by the affected population. Among commercial FSOC, those derived from food sources are usually perceived by consumers as natural and harmless. This appreciation is stimulating their acquisition through channels other than those of regular (i.e., subjected to rigorous quality controls) commerce, including e-commerce from third under development (or even unidentified) countries. Although some of these FSOC has been associated to different health benefices [1], their consumption has also been linked to several food and medical alerts [2] followed by (temporary) withdraw from commerce.

This follow-up study reports on the concentration of phthalates previously identified on capsules of dietary supplements commercialized for overweight control and based on food sources [3]. In particular, 8 phthalates identified by non-orientated comprehensive two-dimensional gas chromatography-time of flight mass spectrometry on capsule extracts obtained after minimal sample treatment (i.e., 10 min ultrasounds extraction of 0.30 g of FSOC capsules with 3 mL of *n*-hexane) have now been subjected to specific (i.e., target) analysis using a previously optimized methodology based on ultra-high performance liquid chromatography coupled to triple quadrupole tandem mass spectrometry (UHPLC-QqQ(MS/MS), using an ESI interface and a BEH phenyl column [4]. Levels of phthalates on the capsules of the six evaluated food-based FSOC are reported and the phthalates profiles evaluated and discussed.

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P-FA-08

MONITORIZATION OF PHENOLIC COMPOSITION OF MANGO PEEL (*Mangifera indica*) by HPLC-DAD-q-TOF-MS DURING FIVE RIPENING STAGES

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Mango industry processing generates high quantities of mango by-products such as peels which contain different families of phenolic compounds with bioactive properties for the human health [1]. Therefore, the possibility of recovering these valuables compounds could be of great interest of food, cosmetic and nutraceutical industries.

Despite the previous characterization of phenolic profile of mango peel, it was only made on mangoes at the optimal consumption ripeness [2]. However, based on the color changes, it is supposed that phenolic composition of mango peel varies during the maturation process. For that reason a monitorization of phenolic compounds during different ripening stages is crucial to elucidate the optimum stage for the recovery of bioactive compounds.

With this aim, phenolic compounds of mango peels from Keitt variety during 5 ripening stages was isolated by means of ultrasound assisted extraction. Chemical composition of samples was analyzed by a powerful platform such as HPLC-DAD-q-TOF-MS.

After statistical treatment applied to chemical data, results evidenced the important role of the different ripening stages on the phenolic composition of mango peels. The three earliest stages of maturation showed higher quantities of sinapic, vanillic and digallic acids. Peel samples belonged to the fourth stage of ripening were characterized by greater amounts of quinic, cumaric and ferulic acids, galloylglucose, dihydroxybenzoic acid, hydroxybenzoil galloylglucoside and trigalloylglucose. Meanwhile those samples from over-ripening stage exhibited major quantities of galloyldiglucoside, dihydroxybenzoic acid, hexa- and heptagalloylglucose, catequin and quercetin.

Therefore, ripening stage must be taken into account in order to maximize the recovery of target bioactive compounds.

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P-FA-09

EMULSION TECHNOLOGY FOR THE DEVELOPMENT OF FUNCTIONAL OILS

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Functional foods represent one of the most intensively investigated and widely promoted areas in the food industry and nutrition sciences today [1]. In this context, *Hibiscus sabdariffa (H. sabdariffa)* is one of the most promising emerging natural sources to be incorporated in many functional foods due to its healthy properties [2]. These effects have been attributed to its chemical composition, mainly based on phenolic compounds i.e. hibiscus acid, chlorogenic acid, anthocyanins, quercetin or kaempferol [3]. However, it should not be forgotten that these phenolic compounds are unstable and especially sensitive to changes in pH, temperature or atmospheric composition. This chemical instability characteristic makes necessary to preserve them from agents such as light, oxygen, temperature, or even gastric residence time. Consequently, functional food formulation using water in oil (W/O) emulsions appears as an available and scalable technique to carry out this challenge that could allow the prolongation of the shelf life antioxidants extracted from *H. sabdariffa.* In the current work, new functional oils (extra virgin olive oil, EVOO and sunflower oil, SO) containing antioxidants from *H. sabdariffa* extract were developed by W/O emulsion and their chemical stability was analyzed over time. The results showed that EVOO emulsions were chemically more stable over time than SO emulsions in terms of total phenolic content (TPC), antioxidant activity and chemical composition measured by HPLC-ESI-TOF-MS. In addition, the antioxidant activity obtained by TEAC remained constant during 30 days. Thus, W/O emulsion technology has proven to be a potential method to vehiculize and stabilize bioactive compounds from *H. sabdariffa* into edible oils.

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P-FA-10

QUALITATIVE AND QUANTITATIVE DIFFERENCES ON THE PHENOLIC PROFILE OF PLE LEAVES EXTRACTS OBTAINED FROM FOUR *MORUS ALBA* VARIETIES

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Morus, also known as mulberry, is widely distributed in Asia, Europe, North and South America and Africa since it has a great genetic variability and adaptability to different environmental conditions, enabling its crop in diverse locations [1]. *Morus* is a botanical genus which content 24 species, being white mulberry (*Morus alba*), black mulberry (*Morus nigra*) and red mulberry (*Morus rubra*) the most commonly known. Among these, *Morus alba* has been traditionally used in infusions to alleviate different illnesses such as fever or strengthen joints due to its antibacterial, antioxidant or hypoglycemic activities [2]. These beneficial properties have been related to their phenolics which can be distributed in phenolic acids and flavonoids among others. All these bioactive compounds have pointed out the potential use of their leaves for developing functional foods. For this reason, the aim of this study was to know the qualitative and quantitative differences among four varieties of *M. alba* (Filipinas, Kokuso, Valenciana and Cristiana). To achieve this goal, Pressurized Liquid Extraction was used to retrieve phenolic compounds from leaves. This Green technology ensures a great extraction yields using GRAS (Generally Recognized as Safe) solvents. In order to characterize and to quantify, High Performance Liquid Chromatography coupled to a time-of-flight mass spectrometer (HPLC-DAD-ESI-TOF) was applied. As result, 50 compounds belonging to three different chemical groups were characterized: phenolic acids, flavonoids and fatty acid derivatives. The quantitation of identified compounds shown statistical differences between varieties opening a promising investigation field with regard to bioactivity.

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P-FA-11

RECOVERING OF ANTI-INFLAMATORY AND ANTI-OBESOGENIC COMPOUND FROM *LIPPIA CITRIODORA* LEAVES BY SUB-CRITICAL FLUIDS EXTRACTION

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Genus *Lippia* includes approximately 200 species and originated in South America [1]. They have been traditionally used for their healthy properties. *Lippia citriodora,* in particular, has been used to prepare infusions and beverages to treat some diseases such as fever, stomachache or indigestion as well as anti-inflammatory or diuretic applications [2]. Many of these beneficial effects are attributed to phenolic compounds containted in their leaves. In particular, verbascoside (also known as acteoside) belongs to phenylpropanoids group which has been related to beneficial effects such as anti-obesogenic compound acting as AMPK (AMP-activated protein kinase) modulator [3]. These properties together with the consumer interest to intake natural food to improve its life style, have addressed the study of innovative extraction techniques to improve the recovery of phenolic compounds from botanicals and obtain enriched extracts in particular compounds. On this scenario, Pressurized Liquid Extraction (PLE) is an environmentally-friendly extraction technique with very short extraction times claimed to provide great yields. Thus, in this study, a Response Surface Methodology was applied to optimize the recovery of verbascoside using PLE system. To achieve this goal, a Central Composite Design 2^3 model with center and star points was performed using as independent variables temperature, extraction time and percentage of solvent (ethanol and water) whereas response variables were extraction yield, and verbascoside concentration. Quantitation of this phenylpropanoid present in each extract was carried out by High Performance Liquid Chromatography coupled to electrospray Time-of-Flight Mass Spectrometrer using a validated method. As a result, PLE optimization enabled the attainment of enriched extracts in verbascoside.

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P-FA-12

DOWNSTREAM GREEN PROCESSES FOR RECOVERY OF BIOACTIVE COMPOUNDS FROM *Porphyridium cruentum*: TOWARDS A MICROALGAL BIOREFINERY

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Biorefinery can be defined as the "development of integrated processes for the conversion of biomass into energy and a variety of products, mainly biofuels and added-value coproducts, in a sustainable approach" [1]. Following this concept, algae-based biorefineries rely on the efficient fractionation of high-valuable/bioactive compounds using algae biomass.

In the present study, a downstream green process was developed for the fractionation of high-valuable bioactives from *Porphyridium cruentum* using different GRAS (Generally Recognized as Safe) solvents. These extractions were performed in sequential steps using (1) subcritical water (Subcritical Water extraction, SWE) and (2) pure ethanol (Pressurized Liquid Extraction, PLE) as solvents. The residue of each extraction step was used as raw material for the next extraction.

During the first step, different number of cycles and temperatures were evaluated in order to maximize the extraction yield of phycoerithrin, the main protein present in this microalga, and to maximize the content in sulfated polysaccharides. Furthermore, optimization of the final step (2) was performed with the objective of recovering the highest content of carotenoids. Finally, results show that the optimal temperature to maximize carotenoid content was 125 ºC. All ethanolic fractions were characterized by chromatographic techniques coupled to mass spectrometry (HPLC DAD-APCI-MS/MS). In these sense, zeaxanthin and β-carotene were the main carotenoids in ethanolic extracts.

In conclusion, a selective fractionation of high added-value compounds was achieved using the proposed green downstream platform. Potentially, these bioactives might be used in the food, pharmaceutical and cosmetic industries.

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P-FA-13

USE OF COMBINED ANALYTICAL TECHNIQUES TO PREVENT LABELLING FRAUD OF IBERIAN HAM

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Iberian dry-cured ham is a highly appreciated product from Spain. It is officially classified in 4 commercial categories according to the pig's breed purity and feeding regime. These categories reach very different prices in the market, which promotes labelling fraud, causing great damage to farmers and food sector. Current Spanish legislation does not include any official method for Iberian ham authentication; however, a standardized analytical method could serve the authorities to fight against fraud and to provide guarantees for costumers. For this purpose, Raman spectroscopy was studied as a screening technique to classify Iberian dry-cured ham depending on the pig's feeding regime and breed. Slices of 110 hams of different categories were analyzed. Samples' Raman spectra showed high levels of fluorescence and ordinary bands were not clearly defined. However, with chemometric treatment it was possible to extract non-apparent information. Classification groups were obtained with classification rates ≥ 83% for breed and feeding regime just employing fluorescence spectra. In addition, a gas chromatography (GC) column coupled to ion mobility spectrometry (IMS) was employed as a complementary technique to confirm the results provided by the screening technique. Slices of 81 hams of different categories were sampled and analyzed following a previously developed method [1]. Due to the two-dimensional nature of GC-IMS measurements, great quantities of data were obtained. Thus, a chemometric approach based on the selection of individual markers that appeared throughout the spectra was required to obtain the final chemometric models. Classification groups with a 100% classification rate were obtained for feeding regime. The described results show that Raman could be successfully used as a screening technique and GC-IMS as a verification technique. A non-invasive ham sampling method for GC-IMS analysis was also studied with this same aim. A standard needle was used to extract small fat quantities from ham before opening it; just pricking with the needle. The potential of this new methodology was demonstrated sampling and analyzing 120 Iberian hams from different categories. Subsequently, 2 chemometric models were obtained for differentiation of breed and feeding regime, which provided validated classification rates ≥ 92%. In addition, several markers employed were identified to facilitate method transference between laboratories [2].

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P-FA-14

HS-GC-IMS AS A POWERFUL ANALYTICAL TOOL TO CLASSIFY OLIVE OIL: EXPLORING DATA TREATMENT AND CHARACTERISTICS OF TWO DEVICES

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In this work, the potential of head space (HS)-gas chromatography (GC) coupled to ion mobility spectrometry (IMS) for the mapping of olive oil volatiles organic compounds (VOCs) and classification of different grade of olive oil samples is demonstrated. The dual separation of VOCs in HS-GC-IMS analysis, as a result of their retention characteristics in GC column as well as their mass, size and shape in the IMS detector, involves the generation of a complex multi-dimensional data in each analytical run, whose interpretation is a challenge.

Two chemometric approaches for olive oil classification were compared to classify olive oil samples in an attempt to get the most robust model over time: i) an untargeted fingerprinting analysis by considering all the spectral data and ii) a targeted approach based on peak-region features (markers) from the 3D maps. These chemometric approaches were applied to the analysis of 701 olive oil samples, which were obtained in two olive oil campaigns (2014-2015 and 2015-2016). The models built with data samples of 2014-2015, showed that both chemometric approaches were suitable for olive oil classification (classification rates > 74%). However, when these models were applied for classifying samples from 2015-2016, the classification rates were generally lower, but better values were obtained using markers. The combination of data from the two campaigns to build the chemometric models improve the classification rates (> 90%).

In addition, two GC-IMS devices with different technical configurations were employed; an isothermal HS-GC-IMS and a ramped temperature HS-GC-IMS prototype. Both devices were compared in terms of resolution, precision and classification rates using a 30 m non-polar capillary column. Our results suggested that the resolution was improved using a ramped temperature HS-GC-IMS prototype. The repeatability values (RSD) for the quality control standards were lower than 10 % in both cases. In order to improve more the resolution, a 60 m non-polar column was employed in the ramped temperature HS-GC-IMS with also adequate repeatability. Moreover, a targeted chemometric processing was carried out to evaluate the latter methodologies for olive oil classification using 91 samples. The classification rates were up to 100 % depending on the analytical method and the calibration model.

P-FA-15

IS GC-IMS A SUITABLE INSTRUMENT FOR ROUTINE ANALYSIS?

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Gas chromatography (GC) is one of the most common analytical techniques in routine laboratories, mainly coupled to flame ionization or mass spectrometry as detectors. Ion mobility spectrometry (IMS) is an analytical technique used to separate and identify ionized molecules in gas phase based on their mobility in a carrier buffer gas [1]. It is already used by security forces for detection of toxic substances, explosives and drugs [2]; but it is not well known in other analytical fields. IMS devices are extremely sensitive and can be coupled to a gas chromatography column in order to improve its selectivity and to achieve a multi-dimensional separation. Using the coupling of GC to an IMS, several applications have been developed in the field of agri-food quality [3]. However, GC-IMS is not widely commercially available despite having several advantages compared to other conventional couplings: it does not require sample pre-treatment, it is relatively cheap, and it provides reproducible results. There are some companies which offer IMS as detector to GC. But since there is a lack of scientific studies which demonstrate the potential of this device in a routine lab, the potential market to sell GC-IMS is very small. Nowadays, no official organism employs GC-IMS for routine analysis and it is not considered in current regulation. In this work, we have elaborated a quality control procedure to monitor the validity of the results obtained with a GC-IMS following the recommendation included in the UNE-EN ISO/IEC 17025:2005 established in point 5.9.1. The validation procedure requires the study of diverse analytical properties: selectivity, sensitivity and robustness. In this work, the suitability of GC-IMS for routine analysis has been evaluated analysing more than 500 olive oil samples over a period of 6 months. The quality control procedure followed during these months have involved a systematic day-to-day checking continuous monitoring data to decide whether the obtained results are reliable or not. The procedure involves analysis of blanks, external standards, quality control samples and the evaluation of internal standards added to all olive oil samples analysed. Moreover, it has been developed a procedure to transfer a calibration equation from one device to another which permit classify unknown samples based on chemometric information obtained using selecting chemical markers.

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P-FA-16

TOWARD THE VALORIZATION OF CURUBA (*Passiflora mollissima* (Kunth) L. H. Bailey) SEEDS: SUSTAINABLE EXTRACTION AND CHEMICAL CHARACTERIZATION

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Passiflora mollissima (Kunth) L. H. Bailey is a native plant from South American Andes used in food and folk medicine. *P. mollissima* fruit, commonly named curuba or banana passion fruit, is an exotic product of growing consumption by its organoleptic properties and functional value [1]. Curuba is a good source of vitamins, minerals, fiber, and bioactive phytochemicals such as carotenoids and polyphenols, among others [2]. The industrial processing of curuba generates wastes such as peel and seed, accounting for approximately 30% of the whole fruit in the case of seeds. Considering that wastes disposal represents environmental and economical problems for the food processing industry, the utilization of curuba seeds under a valorization strategy would be an innovative and sustainable alternative.

Hence, considering the bioactive potential of this food by-product, a valorization strategy based on a sequential pressurized liquid extraction (PLE) procedure was optimized in order to obtain polyphenolic-rich extracts from curuba seeds with the highest antioxidant capacity. In the first step, seeds were defatted evaluating different non-polar solvents (*n*-Hexane, *n*-Heptane, *n*-Cyclohexane and *d*-Limonene) under PLE conditions. In the second step, ethyl acetate and ethanol were used as extraction solvents at different temperatures to obtain polar extracts. The optimal extracts were first characterized by LC-q-TOF, allowing tentative identification of the major phenolic components. In order to have complementary information of the extract's composition, the volatile fraction was analyzed by GC-q-TOF.

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P-FA-17

HPAEC-PAD ANALYSIS OF FERMENTATION SELECTIVITY OF NEWLY SYNTHESIZED OLIGOSACCHARIDES BY HUMAN-DERIVED BIFIDOBACTERIAL SPECIES

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There is currently a high scientific and commercial interest in finding efficacious applications of the concept of prebiotics which aim to beneficially modulate gut microbiota composition and associated bacterial metabolic activities. Bifidobacteria have frequently been the microbial target of prebiotics as they represent commensal bacteria of the human gastrointestinal tract with many purported beneficial activities.

Several studies have demonstrated that dietary fibers, especially non-digestible oligo-/poly-saccharides, alter the number and/or activity of particular elements of the gut microbiota, thereby leading to improvements in host health [1]. Significant scientific efforts are ongoing to identify novel and possibly improved compounds that possess such beneficial or prebiotic potential.

In this context, the present study evaluated the *in vitro* pure culture fermentation properties of *Bifidobacterium breve* UCC2003 and *B. longum* NCIMB 8809 on several purified oligosaccharides, namely 4-galactosyl-kojibiose, lactulosucrose, lactosyl-fructosides (LFOS), raffinosyl-fructosides (RFOS) and galactooligosaccharides derived from lactulose (GOS-Lu), which were obtained by enzymatic synthesis using microbial transglycosidases [2-6]. HPAEC-PAD was a powerful technique for monitoring oligosaccharide consumption by these bifidobacterial strains. Our results demonstrate that the two assessed bifidobacterial strains preferentially metabolized oligosaccharides with a degree of polymerization of 2 and 3, although monomer order and type of glycosydic linkage also appear to play a role in fermentation selectivity.

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P-FA-18

BEHAVIOR OF PECTIN DURING *IN VITRO* GASTROINTESTINAL DIGESTION AND EFFECT ON HUMAN COLONIC MICROBIOTA

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Regulation of the microbiota through the consumption of prebiotics is a well-known concept nowadays. As it has been defined, prebiotics are a group of compounds with limited digestion that are selectively fermented by the gut microbiota conferring health benefits to the host [1]. In this regard, pectin and its derivatives could be considered as prebiotic candidates [2]. To evaluate this potential , influence on the microbiota has to be elucidated. One of the most relevant methodologies to determine the influence of potential prebiotics on the microbial composition is the quantitative polymerase chain reaction (*q*PCR), method which allows us to quantify the microbial population of bacteria through its DNA. In order to monitorise the behavior of pectin through the gastrointestinal tract, HPLC methods are considered the most useful technique due to its simplicity, selectivity and reliability [3]. In this sense, the aim of this work was to evaluate the degradation of a commercial citrus pectin during the gastrointestinal digestion in a dynamic gastrointestinal simulator (simgi®), which simulates the stomach (ST), small intestine (SI) and ascendant, transverse and descendant colon (AC, TC, DC) by Size Exclusion Chromatography (HPLC-SEC), and the influence on the microbial composition by *q*PCR. Citrus pectin samples were added to a nutritive medium (30 g/L) and were subjected to gastrointestinal digestion using the simgi®[4]. Samples were withdrawn from all compartments during 5 weeks and, then, were centrifuged at 13,000*g* for 5 min; supernatant from feeding period was used for HPLC analysis of digested pectin whereas pellets were used for DNA extraction and bacterial quantification. TSK-GEL column G5000 PWXL. 7.8 x 300 mm, particle size 10 µm and G2500 PWXL, 7.8 x 300 mm, particle size 6, were consecutively used for the analysis and QIAamp DNA Stool Mini kit and ViiA7 PCR Systems were used for bacterial DNA extraction and detection, respectively. Pectin showed almost no changes in ST and SI when compared to the initial samples, whereas fermentation in the three colon compartments showed a high degradation with an increasing presence of low molecular weight carbohydrates (<18 kDa). Significant increase in *Bifidobacterium, Bacteroides, Faecalibacterium prausnitzii* and *Enterobacteriaceae* was observed after feeding with citrus pectin and an overall decrease was observed after the washout period. These results emphasize the potential benefits of pectin on gastrointestinal system even though further *in vivo* studies should be conducted.

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P-FA-19

DETERMINATION OF SELECTED PHARMACEUTICALS IN LETTUCE CROPS BY HRMS X500R Q-TOF

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Climate change is altering our lifestyle and our relationship with the environment. One of these changes is the reuse of wastewater for agricultural purposes, mainly in arid and semiarid areas worldwide [1]. This practice is a great source of contamination in crops due to the incomplete elimination, among others, of emerging organic pollutants, such as pharmaceuticals and their human metabolites, during sewage treatment in wastewater treatment plants (WWTPs). Furthermore, processes taking place on WWTPs can, sometimes, transform these compounds into others, instead of eliminating them and reaching a complete mineralization. These compounds can be uptaken up by plant roots from soil and assimilated by crops [2]. The uptake pathways, bioaccumulation and translocation processes are still unknown.

The aim of this work was to develop analytical methodologies for the extraction and determination of selected pharmaceuticals in lettuce leaves, analyzed by HRMS X500R Q-TOF (Sciex). For this purpose, lettuces were grown in pots under controlled conditions of temperature or sun exposure. They were irrigated with tap water spiked with high concentrations of selected compounds (100 ng mL-1), during 30 days. Control plants were irrigated with tap water, free of standards.

Lettuce samples were recollected, cleaned from soil and lyophilized. Later, samples were homogenized and extracted with QuEChERS extraction salts. Extracted fractions were evaporated and reconstituted into a mix of water:methanol (90:10) and analyzed by LC-HRMS. Preliminary results showed the presence of ibuprofen, diclofenac and triclosan in the samples.

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P-FA-20

STUDY OF PEPTIDE COMPOSITION IN COFFEE SILVERSKIN PROTEIN HYDROLYSATES SUBMITTED TO DIFFERENT ROASTING PROCESSES BY LC-ESI-QTOF

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Coffee silverskin is one of the by-products formed during roasting of coffee beans. In fact, high amounts of this by-product are produced by roasters in industry. Even though coffee silverskin is employed as fuel or for composting, different works have pointed out that it presents antioxidant properties (attributable to its phenolic composition) and has hyaluronidase inhibition activity and prebiotic properties [1,2]. Previous studies show that coffee silverskin contains proteins (16.2-19 %), fat (1.56-3.28 %), minerals (7 %) and dietary fiber (50-60 %), among others. However, this by-product is a relatively unexplored source of bioactive compounds. In fact, till now, there are no studies focused on the extraction and identification of peptides from coffee silverskin.

The purpose of this work was to investigate the peptide composition of protein hydrolysates from *Arabica* coffee silverskin submitted to three different roasting degrees in order to evaluate the possible changes that this process could produce in peptide composition. With this aim, an analytical methodology was developed enabling the extraction of soluble proteins for their subsequent precipitation and enzymatic digestion of the extract, LC-ESI-QTOF analysis, and *de novo* sequencing. Different protein extraction procedures were evaluated using pressurized liquid extraction (PLE) and conventional methods. Moreover, several enzymes, such as Alcalase or Thermolysin, among others, were tested in order to produce small peptides with potential bioactivity (2-20 amino acids). Then, the antioxidant activity of protein hydrolysates was studied using different assays, and finally, the separation and identification of peptides in different roasted silverskin samples was carried out.

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P-FA-21

MALDI-TOF MS ANALYSIS OF PROCYANIDINS DERIVED FROM *VITIS VINIFERA* L. SEEDS DISAGGREGATED BY ULTRASOUND

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Proanthocyanidins, known also as polyflavan-3-ols or condensed tannins, are the second most abundant natural phenolics in plants and consist of mixtures of oligomers made of flavan-3-ol monomeric units linked mainly through C-4 and C-8 or C-6 bond, being procyanidins (PCs) the most widespread group [1]. Beyond contributing to organoleptic characteristics of foods they are responsible for some bioactive properties such as cardiopreventive, anti-inflammatory, antioxidant, antiallergic, antithrombotic, antibacterial and anticarcinogenic activities, among others [2]. Rapid structure determination of these compounds is needed, notably for the more complex PCs. Matrix-assisted laser desorption/ionization-time-of-flight mass spectrometry (MALDI-TOF MS) has been proved to be effective in the structural determination of these polymers related to grape seeds, in spite of the presence of other food components which may affect signal intensities [3]. Power ultrasound (US) (>1 W/cm^2) has been pointed out as an adequate environmental friendly physical technique to improve the miscibility of solution and suspensions and depolymerisation of biomacromolecules [4]. To the best of our knowledge, no investigation has been done on a previous treatment of complex polymeric procyanidins before MALDI-TOF MS structural elucidation. In this work, we have subjected to US (45 and 20 kHz) a purified macromolecular fraction (more than 85% of polymeric PCs) from grape seed extract obtained by preparative tangential-flow pressure-driven ultrafiltration and diafiltration with water. MALDI-TOF MS analysis showed the occurrence of 6 B-type and 4 A-type procyanidin series in this fraction. The presence of 1.2% (w/w) of protein by colorimetric assay of Bradford, as well as minor concentrations of sorbitol, fructose, glucose and *myo*-inositol were also determined by GC-FID. US treatments gave rise to a substantial increase (<50%) of catechin and oligomeric and polymeric procyanidin content. US at 45 kHz produced also an important rise in the amount of PCs with higher molecular masses (up to decamers) and a broad increase in the mass signal intensities in most of the detected B-type procyanidin series. In general, US produced certain deliverance of monomeric, oligomeric and polymeric procyanidins that most probably proceed from disaggregation of linkages with other biopolymers, such as proteins and/or polysaccharides. The most practical application of this study was that US could be a very useful procedure for improving the analysis of polymeric PCs by MALDI-TOF MS.

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P-FA-22

CHROMATOGRAPHIC CHARACTERIZATION OF PECTINS EXTRACTED FROM ARTICHOKE BY-PRODUCTS USING ULTRASOUNDS

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Pectin is one of the most structurally complex families of polysaccharides in nature and is widely used as functional food ingredient due to its technological and biological properties. The majority of pectin used is extracted from by-products of citrus peel, apple pomace and sugar beet pulp, however currently there is an interest in use alternative sources such as artichoke by-products. Extraction methodology exerts great influence on pectin structure. Although chemical extraction using strong acids and high temperature is used in the industry [1], other innovative techniques are being searched, such as ultrasound (US) assisted extraction, which can be combined with the use of enzymes [2]. Therefore, the aim of this work was to do a GC-FID and HPSEC-ELSD characterization of pectin extracted from artichoke by-products using different methods. Chemical extractions were carried out employing nitric acid and sodium citrate. For enzymatic extraction, Celluclast preparation was chosen and US assisted extractions, with and without enzyme, were performed on pulsed mode with a probe. Molecular weight distribution and monomeric composition of pectin were determined by HPSEC-ELSD and GC-FID, respectively.

According to the results obtained, the highest extraction yield was achieved when US were used in combination with enzymes (11.3%). With regard to average molecular weight of pectin, US-extracted pectins showed lower values (124-133 kDa) than pectin extracted with a combination of US and enzymes (160-233 kDa) and acid-extracted pectin (146-238 kDa). Galacturonic acid (GalA) content was higher in pectin extracted with acids (79.6-88.3%) while the degree of branching [Rha/GalA], linearity pectin backbone [(Rha+Ara+Gal)/GalA] and degree of extent of rhamnogalacturonan I [Rha/(Ara+GalA)] (0.05, 0.47 and 0.04, respectively) were higher in pectin extracted with US and US and enzyme Regarding pectic neutral sugars, rhamnose (Rha) ranged from 2.0 to 3.2% while galactose (Gal) and arabinose (Ara) contents were higher in pectins treated with US and US with enzyme for prolonged times (6.0-6.2% and 15.2-17.4%, respectively). Xylose was found only in enzymatically extracted pectin (0.4-1.4%). On the other hand, glucose from other polysaccharides co-extracted with pectin was higher when US were applied (8.4-11.5%) and also unknown monosaccharides (6.2-10.0%) were present. These results indicate that application of US in combination with enzymes gave rise pectins structurally different with respect to those obtained by conventional methods and with possibility to use them as functional ingredient.

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P-FA-23

IDENTIFICATION OF BIOACTIVE PEPTIDES AND POLYPHENOLS IN HIGHLY BIOACTIVE EXTRACTS OBTAINED FROM POMEGRANATE (*PUNICA GRANATUM* L.) PEEL BY RP-HPLC-ESI-Q-TOF

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Fruits and vegetables intake has increased significantly worldwide because of their nutritional value and because their consumption is associated with health benefits. Nevertheless, these health benefits have not only be associated to the edible part of the fruit since some studies have revealed that large amounts of phytochemicals and essential nutrients are present in seeds, peels, and other byproducts from fruit industry [1].

Pomegranate peel contains a huge amount of phenolic compounds and their bioactivities have been widely reported. However, the extraction of other compounds such as proteins and peptides has not been studied yet. This work proposes the development of methodologies for the extraction of proteins from pomegranate peel, the evaluation of the capacity of these proteins to obtain bioactive peptides, and their identification by tandem mass spectrometry. Moreover, polyphenol content in extracts will be monitored and its contribution to the whole bioactivity of extracts will be evaluated.

A method based on the use of high intensity focused ultrasounds was optimized and applied to the extraction of proteins from pomegranate peel. Extracted proteins were, next, digested using two different enzymes (Alcalase and Thermolysin) and antihypertensive, antioxidant, and hypocholesterolemic capacity of both hydrolysates was explored. High antioxidant capacity was observed in the extracts but further studies revealed that this capacity was mainly due to the presence of polyphenols and not to the presence of antioxidant peptides. Nevertheless, pomegranate peel peptides were the main contributors to the antihypertensive and hypocholesterolemic capacities observed in both extracts. RP-HPLC-ESI-Q-TOF confirmed the presence of peptides and polyphenols in both pomegranate extracts.

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P-FA-24

ANTIOXIDANT PHENOLIC PROFILE CHARACTERIZATION OF PEEL FROM DIFFERENT *PASSIFLORA* SPECIES BY HPLC-DAD-QTOF/MS

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In the last few years, the development of methodologies for the exploitation of food industry by-products to obtain natural bioactive compounds is an important issue because some by-products can contain high value bioactive compounds. In particular, passion fruits processing industry generates a significant amount of by-products mainly constituted by the peel, which represents more than half of the fruit [1]. Although *Passiflora* peel is the least studied by-product from this fruit, the scarce information available about passion fruit peel suggests that this by-product could be a potential source of antioxidant phenolic compounds with health-promoting effects [2]. In the search of new environmentally clean extraction processes to extract these bioactive compounds, pressurized liquid extraction (PLE) is gaining attention. PLE shows important advantages compared to traditional extraction processes.

In this work, PLE using mainly water as extraction solvent was carried out to extract antioxidant phenols from passion fruit peels from four different species (*P. edulis*, *P. edulis* flavicarpa, *P. mollisima* and *P. ligularis*). Additionally, the antioxidant capacity and the total phenolic content of the extracts were measured by trolox equivalent antioxidant capacity (TEAC), 2,2-diphenyl-1-picrylhydrazyl (DPPH) and Folin-Ciocalteau assays. In order to identify the compounds responsible of the antioxidant capacity observed, a high-performance liquid chromatography method with diode array and quadrupole time of flight mass spectrometry (HPLC-DAD-QTOF/MS) detection was developed. Tentative structural elucidations of 58 phenolic compounds were obtained. To the best of our knowledge, this is the first time that many of the phenolic compounds identified in this work have been characterized in different species of *Passiflora* peel. Flavones, chalcones and phenolic acids were the main classes of polyphenols that may contribute to the total antioxidant capacity of the *Passiflora* peel extracts.

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P-FA-25

A CAPILLARY-LC-IT-MS/MS METHODOLOGY FOR THE QUANTITATION OF FOUR ACE-INHIBITORY PEPTIDES IN *PRUNUS* SEED HYDROLYSATES

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Seeds from *Prunus* genus fruits have demonstrated to be a source of highly angiotensin-converting enzyme (ACE)-inhibitory peptides after digestion of their protein extracts with Thermolysin enzyme. Previous studies on plum, peach, and cherry seeds revealed that peptides IYSPH, IYTPH, IFSPR, and VAIP presented high ACE-inhibition that could be related to the high activity showed by their hydrolysates [1, 2, 3]. With the aim to evaluate which *Prunus* seeds were more profitable to obtain these peptides, this work has been devoted to the development of a capillary-LC-ESI-IT-MS/MS method enabling their simultaneous quantitation in different fruits and varieties from *Prunus* genus. Peptides were separated by RP-HPLC using a binary gradient (5-26% ACN + 0.3% (v/v) acetic acid) in 20 min. Different parameters related to the ESI source (capillary voltage, end plate voltage, nebulizer pressure, dry gas flow, and dry gas temperature) and the IT performance (ion charge control (ICC) target and collision energy) were optimized for each peptide. This optimization enabled to increase the sensitivity up to a 75% in the case of peptide IYSPH. The validation of the method revealed that the methodology was sensitive, selective, precise, accurate, and free of matrix interferences. The developed methodology was successfully applied to the determination of the four peptides in seed hydrolysates from 16 different Prunus genus fruits: peaches (7 varieties), plums (2 varieties), nectarines (3 varieties), apricots (2 varieties), cherry, and paraguayo. Peaches and plums seed hydrolysates presented the highest peptides concentrations while paraguayo hydrolysate showed the lowest. A high correlation was observed between the concentration of the four ACE-inhibitory peptides, suggesting that they could have been released from the same proteins. Differences in peptides concentrations partially explained the differences in the ACE-inhibition of the hydrolysates, although results suggested that this activity could have been influenced by other non-quantified peptides.

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P-FA-26

HEADSPACE SOLID-PHASE MICROEXTRACTION GAS CHROMATOGRAPHY-MASS SPECTROMETRY FOR THE DETERMINATION OF SEMI-VOLATILE FLUORINATED COMPOUNDS IN MICROWAVE POPCORN BAGS

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Perfluoroalkyl and polyfluoroalkyl substances (PFASs) constitute a huge group of organic compounds, which are characterised by a fully or partially fluorinated carbon chain. Among them, fluorotelomer alcohols (FTOHs) and olefins (FTOs), perfluorooctanesulfonamide (FOSA) and perfluorooctanesulfonamide ethanol (FOSE), have drawn growing attention due to their distribution and mobility in the environment and their capability to be degraded into more persistent organic pollutants, such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). These families of semi-volatile compounds have been used as substitutes of PFOS and PFOA in a wide range of applications, such as fire-fighting foams, impregnating agents, coatings and packaging materials. Nevertheless, there are few data about their occurrence in food packaging materials making necessary the development of reliable and sensitive analytical methods for their determination [1,2].

In the present work, a fast and simple analytical method for the simultaneous determination of semi-volatile PFASs, including FTOHs, FOSAs, FOSEs and FTOs, in microwave popcorn bags based on headspace solid-phase microextraction (HS-SPME) combined with gas chromatography-mass spectrometry (GC-MS) has been optimised and validated. Before the HS-SPME procedure, the analytes were released from the packaging material using an ultrasound-assisted extraction (UAE). Among the solvents tested, methanol was found to be the most effective to achieve maximum sensitivity. To establish the optimum HS-SPME conditions for an adequate extraction of the target compounds, a central composite design was employed. Quality parameters of the developed UAE HS-SPME GC-MS method were determined, providing good linearity, high precision (RSD % < 13 %) and trueness (RE (%) < 15%). In addition, the method allowed the detection of the target compounds at very low concentration levels with limits of detection ranging from 0.002 ng cm^{-2} to 0.1 ng cm^{-2}. Finally, the developed method was applied for the analysis of several microwave popcorn brands (before and after cooking), obtained from different local supermarkets. Among the analysed samples, 6:2 FTOH was the most frequently detected compound at concentrations ranging from 0.02 ng cm^{-2} to 4.9 ng cm^{-2}. Moreover, the cooking process and the presence of additives in the popcorn bags, such as salt, butter or sugar, seemed to have a significant influence on the concentration, as they might promote their detachment from the coating.

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P-FA-27

DEVELOPMENT OF DISPERSIVE SOLID PHASE EXTRACTION METHOD FOR THE ANALYSIS OF PHOTOINITIATORS IN FATTY FOOD BY UHPLC-MS/MS

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Packaging materials are widely used to preserve and guarantee food quality, but also for marketing purposes. However, food packaging is also one of the potential sources of food contamination that concerns society, since packaging material constituents can migrate into food and some of migrating substances have shown endocrine-disrupting effects in humans. However, metabolism and detoxification in babies are not as efficient as in adults so the presence of these contaminants in baby food is of great concern. Benzophenone and its derivatives (BPs) are a family of compounds commonly used as photoinitiators and additives to improve the characteristics of plastic packaging materials that can potentially migrate into food. Thus, the aim of this work is to develop an analytical method for the determination of seventeen BPs in baby food products of high fat content [1]. The chromatographic separation of 17 BPs was achieved using an Accucore C18 (150x2.1 mm, 2.6 µm) column at 35ºC and a ternary mobile phase of methanol:acetonitrile:water (formic acid/ammonium formate, 25 mM, pH 3.75) at 600 µL min^{-1}. This chromatographic method was used for the determination of BPs by UHPLC-HESI-MS/MS in MRM mode. Moreover, the suppression/enhancement of ionization was studied in the HESI source between the compounds that coelute in the chromatographic separation. Under these conditions, instrumental limits of detection (ILODs) have been estimated and they were in the range of 0.01—0.70 µg kg^{-1} for most of benzophenones, except for 44DHBP, BP and HMBP which showed slightly higher instrumental ILOD values (1-2.5 µg kg^{-1}). Regarding baby food sample analysis, the Enhanced Matrix Removal-Lipid (EMR-Lipid) adsorbent was evaluated to be used in the clean-up step and it was tested in three baby food matrices: yogurts, custards and chocolate-based products [2]. The amount of sample, the quantity of dispersive solid phase used and the convenience of dilution or pre-concentration of the extract are some of the critical parameters studied. The EMR-Lipid adsorbent gave the best results with recoveries higher than >65% and the matrix effect was in most cases below 35%, except in yogurt and chocolate product for the most hydrophobic compounds for which matrix effect was greater than 40%. Finally, the clean-up/pre-concentration procedure with the adsorbent EMR-Lipid combined with the UHPLC-HESI-MS/MS method allowed the determination of most of BPs in fatty baby food at concentration levels down to 5—30 µg kg^{-1} in all matrices, except for HOBP that were slightly higher (60—80 µg kg^{-1}). Twenty-seven samples were analyzed and only one sample of chocolate product was positive for MBB and PBZ at a concentration below 0.6 mg kg^{-1}.

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P-FA-28

COMBINED (d)SPE-QuEChERS EXTRACTION OF MYCOTOXINS IN UNIFEED AND ANALYSIS BY HPLC-HRMS

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Mycotoxins are natural secondary metabolites produced by various fungi such as *Aspergillus*, *Penicillium* and *Fusarium*. Some of them can infect crops and produce mycotoxins during cultivation and ensilage. These toxins can cause acute and chronic effects on animal and human health. They are related to severe diseases such as mutagenic, carcinogenic, teratogenic, immunotoxinogenic activities [1] and they can strongly reduce productivity in dairy farms. The European Union (EU) has adopted rules limiting the mycotoxin maximum levels in feeding stuffs, particularly aflatoxin B1, ochratoxin A, deoxynivalenol, zearalenone and fumonisins [2, 3]. In addition, the European Food Safety Authority (EFSA) recommends developing multi-mycotoxin methods because the simultaneous occurrence of mycotoxins and metabolites in feed is commonplace. In this work, more than 20 mycotoxins from different genera were then analyzed in 160 unifeed samples collected in 20 dairy farms.

A sample preparation methodology based on a combination of (d)SPE and QuEChERS extractions was used. Liquid Cromatography-High Resolution Mass Spectrometry was employed by means of a SCIEX TripleTOF® 5600+ equipped with a DuoSpray™ ion source, using Electrospray Ionization (ESI), both in positive and negative modes. A HPLC system (Shimadzu Nexera X2) was used equipped with a Phenomenex Kinetex bioZen™ Peptide XB-C18 (50 x 2.1 mm, 2.6 µm) column at 40°C. The injection volume was set at 10 µl. A powerful workflow based on data-independent acquisition, consisting of fragmenting all precursor ions entering the mass spectrometer in 20-30 m/z isolation windows (SWATH), was implemented.

Analytical performance was evaluated in terms of linearity, repeatability and matrix effect. Relative recoveries were also measured, giving values between 43 and 112%. A matrix-matched calibration was carried out, with R^2 > 0.9957 and enabled reaching the low ppb level (i.e. 1.5 ng g^{-1} for fumonisin B1 or 14 ng g^{-1} for DON). The observed matrix effect, in most cases suppressive, varied amongst mycotoxins and reached in some cases values higher than 80 %. The repeatability was also adequate, showing a relative standard deviation lower than 8.7%.

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P-FA-29

DETERMINATION OF *FUSARIUM* EMERGING MYCOTOXINS IN VEGETABLES MILKS BY UHPLC-MS/MS

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During the last years, mycotoxins (toxic secondary metabolites produced by certain fungi) have become one of the most common contaminants reported worldwide. However, current legislation has established maximum levels only for some well-known mycotoxins (aflatoxins, ochratoxin A, patulin, citrinin, and some *Fusarium* toxins such as deoxynivalenol, zearalenone and fumonisins B1 and B2) and recommendations about the maximum content of T-2 and HT-2 toxins and the presence of ergot sclerotia. These mycotoxins are routinely controlled and analytical methods for their determination are well established. Nevertheless, there are other mycotoxins that are suspicious to be toxic, but have not been extensively explored yet and are not regulated by legislation: the so-called "emerging mycotoxins". Among them, enniantins (ENNs) and beauvericin (BEA), cyclic hexadepsipeptides produced by *Fusarium* spp., comprised a group of great interest, and their frequent presence in food and feed is becoming a matter of concern. Although in vitro studies have showed the toxicity of ENNs and BEA (suggesting genotoxicity and effects on the reproductive system), there are not enough evidences of in vivo toxicity. In this sense, the European Food Safety Authority (EFSA) has concluded that there might be a concern with respect to chronic exposure that should be confirmed by more acute toxicological data.

During the last decade, several studied have revealed the great incidence of these toxins in samples from different countries, mainly cereals. However, the "vegetable milks" or "plant-based milks" (derived from plants, as cereals or nuts) have been scarcely explored regarding mycotoxin contamination. The few studies carried out on these matrices have evidenced the presence of some mycotoxins (including *Fusarium* toxins) in this sort of products although, to the best of our knowledge, no study has been developed concerning emerging mycotoxins. Here, an analytical method based on salting-out assisted liquid-liquid extraction (SALLE) followed by UHPLC-MS/MS is proposed for determination of ENNs A, A1, B, B1 and BEA in rice, oat and soy milks. The method showed good precision and trueness (RSD < 8% and recoveries between 84-97%) with a moderate matrix effect. From a total of 32 samples (rice, oat and rice milks), 3 samples were contaminated with the five mycotoxins, while 5 samples were contaminated with four of them, being oat milk the most susceptible for contamination.

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P-FA-30

DETERMINATION OF MULTI-MYCOTOXIN OCCURRENCE IN FOODSTUFF FROM ALGERIA BY ULTRA HIGH PERFORMANCE LIQUID CHROMATOGRAPHY COUPLED TO TRIPLE QUADRUPOLE MASS SPECTROMETRY (UHPLC-MS-MS)

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Mycotoxins are toxic compounds produced by different types of fungus, belonging mainly to the *Aspergillus, Penicillium* and *Fusarium* genera. European Union has established maximum levels for those mycotoxins considered as chemical hazards in Regulation (EC) 1881/2006 and subsequent amendments. Moreover, methods of sampling and analysis for the official control of mycotoxins were introduced in Regulation (EC) 401/2006. However, other countries have not established any regulation concerning those contaminants, and scarce controls on the products susceptible of contamination are carried out, with the subsequent risk for the consumers.

The aim of this study was to evaluate the mycotoxin contamination of 120 samples of different cereals (maize, rice, wheat and barley) from Algerian markets. With this purpose, a method based on a simple QuEChERS-based extraction and ultra-high performance liquid chromatography coupled to tandem mass spectrometry (UHPLC–MS/MS) was developed. The analytes studied included both regulated mycotoxins in cereals (aflatoxin B1, B2, G1 and G2, ochratoxin A, deoxynivalenol, zearalenone, fumonisin B1 and B2, T-2 and HT-2 toxin), as well as commonly studied mycotoxins (fusarenon-X, citrinin, sterigmatocystin) and emerging mycotoxins (beauvericin and enniatin A, A1, B and B1).

Analytical results showed that 116 out of 120 total cereal samples (96%) were contaminated with at least one toxin. Aflatoxin G1 was the most frequently detected (69 samples, 57%) at concentrations up to 64 µg/kg. Moreover, fumonisins, zearalenone and deoxynivalenol (all of them *Fusarium* toxins) registered very high concentrations, ranging from 4-448877 (FB1+FB2), 9-579 and 23-2055 µg/kg, respectively. In the case of some maize samples, the concentration of fumonisins exceeded in more than 25 times the maximum concentration allowed by EU. Remarkably, 57% of the samples were contaminated with emerging mycotoxins, and in 10 wheat samples the concentration of total emerging mycotoxins (enniatins plus beauvericin) were as high as 2-10 mg/kg. These results alert about the potential risk present in cereals for Algerian consumers regarding mycotoxins, and the necessity of evaluation of the potential toxicity of emerging mycotoxins and their regulation.

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P-FA-31

A PROPOSAL FOR ON-LINE DERIVATIZATION OF AFLATOXINS IN UHPLC WITH FLUORESCENCE DETECTION FOR THEIR DETERMINATION IN RICE SAMPLES

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A fast and simple analytical method has been developed and validated for the determination of aflatoxins (B1, B2, G1 and G2) in rice samples. The procedure is based on a very simple solid-liquid extraction without further clean-up, and subsequent analysis by ultra-high performance liquid chromatography (UHPLC) coupled with fluorescence detection (FLD), using a mobile phase consisting on water and a mixture of acetonitrile and methanol (1:1, v/v), in gradient mode (0 min: 25%B, 0-4 min: 40%B, 4-5 min: 25%B, 5-7 min: 25%B). Fluorescence emission of aflatoxin B1 (AFB1) and aflatoxin G1 (AFG1) were enhanced by post-column chemical derivatization using pyridinium bromide perbromide (PBPB) as reagent. Variables affecting this on-line step, such as size of the reactor coil (length and inner diameter), reaction temperature and reagent concentration and flow rate, were optimized, the last ones by means of experimental design. A three-ways peek "T" connector, with cero dead volume was used to mix the PBPB solution with the eluate coming from the chromatographic column, in order to avoid peak diffusion. A reaction coil of 38 µL, consisting on a peek tube of 3 m length and 0.127 mm I.D., was placed in an oven at a 25 ºC constant temperature, joining the outlet of the "T" connector with the inlet of the FLD cell. The excitation and emission wavelengths for the determination of aflatoxins derivatives were 365 and 460 nm, respectively.

The method was satisfactorily characterized in white and brown rice. Under optimum conditions, external calibration in solvent could be used for quantification purposes, and limits of quantification were well below the maximum contents established by the Commission Regulation (EC) No 1881/2006 for this commodity group. Trueness study was carried out at three different concentration levels, with recoveries in the range of 84.5 % and 105.3 %, and RSDs lower than 5 %.

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P-FA-32

APPLICATION OF CAPILLARY LIQUID CHROMATOGRAPHY TO THE ANALYSIS OF 5-NITROMIDAZOLES IN AQUACULTURE PRODUCTS USING MOLECULARLY IMPRINTED SOLID PHASE EXTRACTION AS SAMPLE TREATMENT

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5-nitroimidazoles (5-NDZs) are a wide-spectrum antibiotic class used for treating infections due to anaerobic protozoan and bacteria. Nevertheless, carcinogenic, genotoxic and mutagenic properties have been attributed to these compounds, and as a consequence, their use in veterinary medicine has been restricted within European countries. Although 5-NDZ residues are not allowed in food of animal origin according to Regulation (EU) No 37/2010, alerts about their presence in animal products destined to human consumption are still notified by the Rapid System of Food and Feed (RASFF) portal. Consequently, analytical methods are required for 5-NDZ determination in order to ensure food safety [1]. In this work, the optimization of a capillary liquid chromatography (CLC) method coupled to UV detection has been carried out. Parameters affecting the separation such as mobile phase composition, mobile phase flow rate, separation temperature and gradient program as well as the type of chromatographic column, have been evaluated. Finally, the separation of eleven 5-NDZ compounds has been performed in a C18 (150 × 0.5 mm, 5 µm) column, using a mobile phase consisted of water (eluent A) and acetonitrile (eluent B) and supplied at a flow rate of 7 µL/min. Column was thermostated at 20°C during the analysis and 320 nm was established as detection wavelength. Furthermore, full loop injection mode (8 µL) was selected and water was considered as injection solvent. Finally, the optimized method has been applied to the analysis of 5-NDZ residues, including three metabolites, in aquaculture products, namely crab, salmon, prawn and swimming velvet crab. A molecularly imprinted solid phase extraction (MISPE) procedure has been applied for sample clean-up, resulting in extraction recoveries higher than 67% for all considered compounds. The method was characterized in all the matrices in terms of linearity ($R2 \geq 0.9964$), precision (repeatability, RSD ≤ 7.9% and reproducibility, RSD ≤ 11.1%) and trueness (recoveries between 80.4 and 108.7%). Decision limits, CCα, ranging from 0.2 to 1.5 µg/L and detection capabilities, CCβ, from 0.2 to 1.8 µg/kg, were obtained [2].

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P-FA-33

DIFFERENT CHEMOMETRICS APPROACHES FOR CLASSIFICATION OF VIRGIN OLIVE OILS USING GAS CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY

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Olive oil is classified according to its quality in extra virgin (EVOO), virgin (VOO) and lampante (LOO). Currently, the oil classification in these three categories is based on sensory evaluation through a panel test, together with some physico-chemical analysis. However, the possible subjectivity of the tasters during the analysis, in addition to the lack of accredited tasting panels outside of Spain, are the main drawbacks of this methodology. In this work, gas chromatography coupled to mass spectrometry (GC-MS) is proposed for the differentiation of these three categories of olive oil as a complementary or alternative method to the panel test.

The analytical method was optimized using 35 standards of volatile compounds previously described in olive oil samples. For the analysis, 1 g of sample was incubated at 140 °C for 15 min and 750 µL of the headspace was injected into a non-polar column (30 m x 0.25 mm id, x 0.25 µm film thickness). The GC temperature was programed with a start temperature of 40 ºC (held for 3 min), which was increased to 250 ºC at 10 ºC/min (held 6 min). The total analysis time for each GC run was 30 min. The ionization was carried out in the electron-impact mode (70 eV) and the data were collected in the range of 20-400 m/z.

The proposed method was used for the analysis of 86 olive oil samples (28 EVOO, 30 VOO and 28 LOO) in duplicate. Firstly, the identification and quantification of the compounds detected in the olive oil samples was carried out in order to establish relationships and differences between the different categories. However, it was not enough for a correct classification of samples, due to the variability within the same category. Therefore, the data obtained with GC-MS were processed using three different strategies: selection of significant markers or peaks, study of the m/z profile, and use of the total ion chromatogram (TIC).

Chemometric models were constructed using 80% of samples and validated with the remaining 20% for each strategy. The best results (87.1% of success) were obtained when the areas of the most representative peaks of the chromatogram were used.

P-FA-34

ANALYTICAL PYROLYSIS OF FISH (*Oreochromis niloticus*) MUSCLE. EFFECT OF DIFFERENT COOKING METHODS

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In this communication a detailed analytical pyrolysis of tilapia fish (*Oreochromis niloticus*) muscle is described. The fish, supplied by Valenciana de Acuicultura (fish hatchery of Valencia, Spain), were acclimatized in the laboratory and for 15 days in two aquariums (8 individuals/aquarium) with 96 L of tap-water at a constant temperature (21 ± 2°C). Fish were fed daily (0.3 g/day) with commercial fish food only (Dibaq S.L., Segovia, Spain). After acclimation, were dissected and each muscle sample was cut into approximately 4 g portions. Fish muscle samples were cooked for 2 min by boiling, steaming, microwaving and broiling. Briefly, for boiling and steaming, the fish muscle was introduced into the pot or onto the food steamer, respectively, with cool water, heated to boiling (100°C) and continued to boil for 2 min. A conventional household microwave oven (Samsung M17-13, 300W, 2450 MHz) was used for microwaving, and samples were broiled in Teflon pans for both sides of the fillet. A non-cooked fish muscle fillet was used as control group. The assays were always carried out by quintuplicate (n=5). All samples were kept at -80°C until freeze dry (Cryodos 80, Telstar, Tarrasa, Spain).

The Py-GC/MS was performed using a double-shot pyrolyzer (Frontier Laboratories, model 2020i, Fukushima, Japan) attached to a GC system (Agilent Technologies, Palo Alto, CA,. USA, model 6890N). The muscle samples (2 mg freeze-dry tissue) were placed in crucible deactivated steel pyrolysis capsules and introduced into a preheated micro-furnace at (350 °C) for 1 min. The volatile pyrolysates were then directly injected into the GC/MS for analysis. The gas chromatograph was equipped with a low polar-fused silica (5%-phenyl-methylpolysiloxane) capillary column (Agilent J&W HP-5ms Ultra Inert, of 30 m × 250 µm × 0.25 µm film thickness. The oven temperature was held at 50 °C for 1 min and then increased to 100 °C at 30 °C min^{-1}, from 100 °C to 300 °C at 10 °C min^{-1}, and stabilized at 300 °C for 10 min, with a total analysis time of 32 min. The carrier gas was He at a controlled flow of 1 mL min^{-1}. The detector consisted of a mass selective detector (Agilent Technologies, Palo Alto, CA. USA, model 5973N) and mass spectra were acquired at 70 eV ionizing energy. Compound assignment was achieved by single-ion monitoring (SIM) for the major homologous series and by comparison with published data reported in the literature or stored in digital NIST 14 (Maryland, USA) and Wiley 7 (Weinheim, Germany) libraries. In a first analytical step, a detailed pyrolysis fingerprint of raw fish muscle tissue is produced and the effect of the pyrolysis temperature from 150 to 550 ºC in 100 ºC increments is studied in both, i) applying each temperature to a different sample or ii) sequentially (multi-shot) applying each temperature to the same sample. In a second phase, after stablishing an optimum pyrolysis temperature of 350 ºC for 1 minute, the effect of the different cooking methods (boil, steam, microwave and broil cooking) in the fish muscle pyrolyzates was studied.

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P-FA-35

IS TENAX AN ADEQUATE SIMULANT FOR THE ANALYSIS OF THE MIGRATION FROM FOOD CONTACT MATERIALS?

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Tenax is the trade name of poly(2,6-diphenyl-p-phenylene oxide), which is used as food simulant for specific migration of dry foodstuffs according to Commission Regulation EU 10/2011 [1] which also establishes specific requirements of plastic materials intended to come into contact with food. These materials and others as paper, ceramic, glass, metal, printing ink and adhesive are in contact with the foodstuff and they are called 'food contact materials'.

However, different studies question the efficiency of Tenax as a food simulant. On the one hand, the migration into Tenax is compared to the migration into real dry foods: semolina pasta, sugar, flour, milk powder and rice. These studies concluded that the migration into Tenax is faster and presents higher values than into the real food [2]. On the other hand, the European Reference Laboratory for Food Contact Materials (EURL-FCM) performed an interlaboratory comparison about the identification and quantification of substances spiked in Tenax and only 48% of the national reference laboratories could identify correctly the substances [3]. In addition, Tenax cannot be recommended as a food simulant for high temperature applications [4].

For this reason, this work has studied the adsorption capability of Tenax obtained in the migration of different plasticizers (butylated hydroxytoluene (BHT), diisobutyl phthalate (DiBP), bis(2-ethylhexyl) adipate (DEHA) and diisononyl phthalate (DiNP)), and benzophenone (BP) into this simulant from different food contact materials. The packaging materials analyzed were: polyethylene (PE) and polyvinyl chloride (PVC) cling-films, paper bread bag, brown paper popcorn bag intended to be heated in a microwave oven and polypropylene (PP) coffee capsules. The analysis was carried out using PARAFAC and gas chromatography/mass spectrometry (GC/MS). BHT, DiBP and DEHA were contained in the Tenax blanks in some of the analyses. The values of the adsorption capability obtained were different depending on the analytes and the materials. In the spiked migration samples, these values ranged from 25.33% to 99.37%.

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P-FA-36

STUDY OF THE MIGRATION OF MELAMINE AND FORMALDEHYDE FROM MATERIALS IN CONTACT WITH FOODSTUFFS WITH HPLC-DAD DATA

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The European legislation has established a specific migration limit (SML) of 15 mg kg^{-1} for formaldehyde and 30 mg kg^{-1} for melamine [1]. Formaldehyde resins are used in the fabrication of melamine kitchenware. Formaldehyde is listed in group 1 so it is carcinogenic for humans [2]. To determine the quantity of formaldehyde and melamine as potential migrants from melamine glasses, a HPLC-DAD method have been implemented. This method is an alternative of the ones proposed in technical guidelines to determine formaldehyde by UV-visible spectrophotometry [3] and melamine by HPLC [4].

Decision limit (CCα) and capability of detection (CCβ) were 0.303 and 0.594 mg L^{-1} for melamine, respectively; and 0.117 and 0.228 mg L^{-1} for formaldehyde respectively, when the probabilities of false positive (α) and false negative (β) were fixed at 0.05.

The migration tests were conducted with simulant B (3% (w/v) acetic acid on water), being the conditions of each exposure 70ºC for 2 hours. The quantity found after the third migration testing [3] was 0.430 mg L^{-1} of melamine and 1.385 mg L^{-1} of formaldehyde for three replicates of three glasses.

Two migration kinetic curves were built for one new glass with the data of sixteen consecutive migrations (70ºC for 30 minutes). The models fitted were: $y = (0.22+0.08x)^2$ for melamine and $y = (-0.37+0.54x^{0.5})^2$ for formaldehyde; being the explained variance, R^2, equal to 99.4% and 99.8%, respectively.

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P-FA-37

A COMBINED LC-UV-MS AND GC-MS APPROACH FOR AUTHENTICATION OF ARTICHOKE (*Cynara scolymus*) SUPPLEMENTS FOR OVERWEIGHT CONTROL

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The consumption of dietary supplements, and especially of those obtained from natural sources, is currently gaining great attention as they are generally considered as a natural alternative to synthetic drugs to treat different conditions. Among them, food supplements from artichoke (*Cynara scolymus*) aimed to overweight control are nowadays one of the most demanded due to the increasing incidence of obesity. However, some of these supplements containing plant-derived bioactives are frequently the target of frauds mainly related to the presence of adulterants in their formulations, discrepancies in the declared content of bioactives, etc. Chromatographic techniques such as gas (GC) and liquid chromatography (LC), coupled to mass spectrometry (MS), are high separation power and sensitive analytical platforms for the analysis of complex mixtures such as those present in artichoke supplements [1]. However, their combined use for authentication of these products has been scarcely explored so far, being this the main objective of the present study.

Twenty-one supplements based on artichoke extracts were acquired in specialized shops, pharmacies and web sites. Moreover, artichoke leaves from different plants were subjected to solid-liquid extraction under different conditions in order to obtain a set of reference extracts. For GC-MS analysis, a 5% phenylmethylsilicone column was used under different temperature program conditions and samples were previously derivatized [2]. Different reverse phase C18 columns and acetonitrile:water gradients were assayed for LC-MS analysis.

GC-MS and LC-UV-MS profiles from reference extracts were fully characterized in order to establish an 'authenticity profile' to be further compared with that of artichoke supplements under study. Whereas the presence of several compounds including low molecular weight carbohydrates, inositols, caffeoyl-quinic acids and flavonoid glycosides was common to both samples, the detection of undeclared compounds (maltodextrins), markers of inappropriate processing or storage (difructose anhydrides) or peaks other than those typical of reference samples in several artichoke supplements might be indicative of their poor quality or even their lack of authenticity.

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P-FA-38

VALORIZATION OF LEGUME BY-PRODUCTS BY EXTRACTING BIOACTIVE INOSITOLS USING A MICROWAVE ASSISTED EXTRACTION PROCEDURE

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There is a great interest in the extraction of bioactive compounds from natural sources to be used as functional food ingredients. Among bioactive compounds, inositols and their derivatives (methyl-inositols, glycosyl-inositols, etc.) exhibit several bioactive properties, mainly associated with insulin resistance activities. These compounds have been detected in edible legume seeds such as chickpeas, lentils, soy beans and mung bean [1, 2].

The interest in the extraction of bioactive inositols is even greater if they are obtained from food byproducts. European companies produce around three million tonnes of legume waste every year. This waste is generally used as animal feed, although its use to obtain proteins and fiber has also been proposed [3]. However, to the best of our knowledge, there are no studies on the composition of inositols in legume waste. Regarding extraction procedures, Microwave Assisted Extraction (MAE) is an efficient extractive technique that usually provides a significant reduction in extraction times and solvent consumption as compared to conventional solid-liquid extraction (SLE). However, this technique has been scarcely applied to the extraction of bioactive carbohydrates and to the best of our knowledge, there is only one study related to the extraction of bioactive carbohydrates from legumes [2]. Therefore, in this work, a MAE method has been optimized to obtain high yields of inositols from soybean (*Glycine max*) pods, as an agro-industrial by-product, and results were compared with those obtained by SLE.

A Box-Behnken experimental design for response surface methodology was used to optimize the MAE method. Extraction time (3-30 min), temperature (50-120°C) and percentage of ethanol as solvent (0-100 %) were considered as variables. Low molecular weight carbohydrates were converted to their trimethylsilyl oximes and analyzed by GC-MS. Optimal conditions (16.5 min, 120°C and 100% water) allowed the extraction of methyl-inositols (57.96 mg/g dry sample) and free *myo*- (1.29 mg/g dry sample) and *chiro*-inositols (1.22 mg/g dry sample). The optimized MAE method resulted to be a good alternative to conventional SLE (60.47 mg/g *vs* 49.64 mg/g dry sample) for the production of enriched inositols extracts from food-grade byproducts.

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P-FA-39

CHARACTERIZATION OF LOW MOLECULAR WEIGHT CARBOHYDRATES AND PHENYLALKANOID GLYCOSIDES OF *Rhodiola rosea* FOOD SUPPLEMENTS BY MULTIDIMENSIONAL GAS CHROMATOGRAPHIC TECHNIQUES

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Rhodiola rosea is a plant belonging to the Crassulaceae family traditionally used in popular medicine, and more recently in the elaboration of different food supplements due to its biological activity [1,2]. These biological properties could be related to the presence of different compounds such as polyphenols, terpenoids, phenylalkanoid glycosides (PAGs) and carbohydrates.

Regarding PAGs, a global estimation of selected bioactives (mainly the phenylpropanoid glycosides rosarin, rosavin and rosin) is usually considered to evaluate *R. rosea* bioactivity. Nevertheless, each of these active compounds shows a specific physiologic effect and, consequently, their individual determination is highly recommended. Studies regarding *R. rosea* roots carbohydrate composition are scarce and, in general, aimed to estimate total and reducing sugars or to the rough determination of free monosaccharides. Therefore, there is a need to develop analytical methodologies that allow the detailed study of the low molecular weight carbohydrate (LMWC) composition of *R. rosea* supplements.

Gas chromatography (GC) is a widely accepted analytical technique for the analysis of complex mixtures. However, as the complexity of the studied mixture increases, the possibility of coelution of target analytes with other compounds or matrix components also increases. In such cases, the incorporation of an additional criterion for unequivocal identification becomes mandatory. This second identification criterion can derive from the hyphenation of GC with a second chromatographic separation technique (e.g., comprehensive two-dimensional gas chromatography, GC×GC) or with a mass spectrometry (MS)-based technique, which provides structural information.

The main objective of the present study was the comprehensive characterization of LMWCs and PAGs of *R. rosea* root supplements by GC-MS and GC×GC-ToF MS to provide a deeper understanding of the composition of these food supplements.

Different *R. rosea* supplements were dissolved in ethanol:water (70:30, v/v), dried under vacuum and subjected to a two-step derivatization procedure using 2.5% hydroxylamine chloride in pyridine (75 °C, 30 min) and trimethylsilylimidazole with trimethylchlorosilane (22 °C, 30 min). These samples were analysed by GC-MS and GC×GC-ToF MS, after optimization of the corresponding chromatographic methods.

In addition to the well-known rosin, rosarin, rosavin and salidroside, other PAGs, carbohydrates, polyalcohols, acids, etc. were determined. Among them, several seven-carbon monosaccharides such as coriose and 2,7-anhydro-β-D-altro-heptulose were detected for the first time in *R. rosea* root supplements. Sedoheptulose was found to be the most abundant compound (13-134 mg g^{-1}), followed by rosiridin (14-118 mg g^{-1}) and rosavin (9-89 mg g^{-1}). The use of GC×GC-ToF MS allowed

the detection and tentative identification of 48 additional compounds mainly belonging to the phenylalkanoid glycoside, pentosyl-hexose and hexosyl-hexose families.

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P-FA-40

A COMPREHENSIVE CHARACTERIZATION OF RASPBERRY KETONE SUPPLEMENTS FOR OVERWEIGHT CONTROL

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Obesity is one of the health problems with greater incidence in developed countries and with a higher economic impact associated with its treatment and that of other related diseases. As a consequence, the use of food supplements derived from plants for overweight control (FSOC) is gaining an increasing acceptance by the consumer who considers them as a natural alternative to prevent or treat this condition. Among the different FSOC commercially available, those including raspberry ketone (4-(4-hydroxyphenyl)butan-2-one) are one of the most demanded. However, the assurance of their potential bioactivity requires their prior authentication. In this sense, the establishment of 'authentication profiles' in which information gathered by different analytical methodologies is combined would be of great usefulness and a topic scarcely addressed so far [1]. In this study, a total of 16 raspberry ketone supplements commercially available and 7 reference raspberry (*Rubus idaeus*) samples from different cultivars were comprehensively characterized by Gas Chromatography coupled to Mass Spectrometry (GC-MS) using a Carbowax stationary phase (30 m x 0.25 mm i.d. x 0.25 µm film thickness). As for the analysis of non-volatile compounds, solid-liquid extraction using solvents of different polarity (dichloromethane and a 80% methanolic solution), followed by a trimethylsilyl oxime derivatization procedure [2] in the case of hydroalcoholic extracts, were used. Volatile composition was determined by Solid Phase Microextraction (SPME) using a Carboxane/Polydimethylsiloxane fiber, according to the method of Soria et al. [3]. First, and in order to establish a 'combined authenticity profile', the different GC-MS profiles (CH_2Cl_2, CH_3OH, derivatized CH_3OH and SPME) from reference samples were fully characterized. In addition to the target bioactive (raspberry ketone), compounds from different chemical families including carbohydrates (fructose, glucose, galactose, *myo*-inositol, etc), terpenoids (linalool, α-ionone, β-ionone), etc. were identified. Second, composition of commercial raspberry supplements was qualitative and quantitatively compared with that of authentic samples. Discrepancies in the content of the declared bioactive together with the unexpected presence of compounds other than those typical of reference samples were determined in several of the supplements under study. Further research should be carried out to confirm the poor quality or even the lack of authenticity of these suspicious products.

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P-FA-41

UNRAVELLING TROPANE ALKALOIDS DEGRADATION FROM BAKED BUCKWHEAT SAMPLES

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Solanaceae plants, which contain huge amount of tropane alkaloids (TAs), can contaminate some food seeds as buckwheat or millet [1]. TAs have pharmacological properties due to their anticholinergic activity and they have potential health risk. Although the presence of these compounds has been widely studied in cereals and pseudocereals, their degradation products or how these compounds can be degraded have not been studied yet.

The aim of this study is the monitoring of the degradation of TAs under real cooking conditions. A total of 17 compounds (amonibenztropine, benztropine, anisodamine, scopolamine, atropine, littorine, aposcopolamine, homatropine, apoatropine, cuscohygrine, calystegine C, calystegine B, calystegine A, scopoline, tropine, tropinone and tropane) were studied. Different fermentation (37˚C and humidity during 1 hour) and baking conditions (37˚C and humidity and 190˚C during 40 min in an oven) were tested. Under these conditions, both vial trials and buckwheat contaminated with Solanaceae seeds were monitored.

To monitor the concentration of TAs in vials and contaminated samples, extraction [2] and chromatographic [3] methods developed previously were used. The results obtained were processed as targeted and untargeted analysis using Compound Discoverer 2.1 and Mass Chem Site 2.0. The processed results indicate that under fermentation conditions the compounds degrade below 50 % and mainly to tropine or tropane, and under baking conditions above 95 % and the compounds were degraded to tropine and tropinone. Besides, some other untargeted tropane alkaloids were detected as convolidine, convolvine or tigloidine and finally some compounds present in the buckwheat matrix as monosaccharides, aminoacids and peptides, and phenolic acids were also detected (as glucose, lysine and chlorogenic acid between others).

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P-FA-42

DETERMINATION OF TRANS-ANETHOLE AND MYRISTICIN IN INFUSION PRODUCTS BY ULTRASOUND EXTRACTION AND GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Currently there is a growing demand for food products prepared from natural sources. This fact is closely linked to the popular belief of consumers that "the natural is equivalent to the healthiest", producing a remarkable increase in the incorporation of spices and aromatic herbs as active ingredients in foods, as food supplements, in infusions and even as condiments.

Alkenylbenzenes are compounds usually present in some herbs and spices, but some of which have genotoxic and carcinogenic effects [1], as trans-anethole and myristicin. Trans-anethole was present in essential oils of green anise (Pimpinella anisum), star anise (Illicium verum) and fennel (Foeniculum vulgare). On the other hand, myristicin can be detected in spices such as nutmeg (seed) or in the mace (wrapped or aril that covers them) of the species of plants called Myristica, and it is especially abundant in Myristica fragrans and in essential oils obtained from it.

Therefore, the human exposure to these substances through the consumption of condiments or through other food products that contain them as flavorings, such as infusions, has increased the need to identify and quantify these compounds by appropriate analytical methods.

In this study, an analytical method was developed and validated for the determination of two alkenylbenzenes, *trans*-anethole and myristicin, in infusion products, which contain spices as anise and nutmeg by gas chromatography (GC) coupled to mass spectrometry (MS). Ultrasound-assisted solid-liquid extraction (UAE) was employed, using ethyl acetate as extraction solvent and an extraction time of 15 min. This method provides acceptable recoveries (94-116 % for *trans*-anethole and 100-115 % for myristicin) and no matrix effect for both compounds was observed. The method is linear at the concentration range 0.02-2.50 mg/kg and provides suitable intra (RSD ≤10 %) and and inter-day precision (RSD ≤14 %). Limits of detection (LOD) was set at 0.5 µg/kg for *trans*-anethole and 1.4 µg/kg for myristicin, whereas the limit of quantification (LOQ) is established at 20 µg/kg for both analytes.

A total of 14 samples were analysed, finding in some of them high values of trans-anethole (1484 mg/kg) and in some samples at concentration of 2 mg/kg, where green anise has not been added. Therefore, its presence could be due to other less common plant components that also contain trans-anethole like mint and licorice.

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All manuscripts will be subjected to the regular selection process for the journal, including the strict peer review procedure; therefore, acceptance for presentation at the meetings is not a guarantee for publication in the journal.

Thanks in advance for your contribution!

Elsevier Team

Conference language

The official languages of the meeting are Spanish and English

Book of Abstracts

The book of abstract can be downloaded from www.secyta2018.es

Oral presentations

Time scheduled for the Plenary Lectures is 40 – 45 min.
Time scheduled for Oral Communications is 20 min (ideally distributed using 15 min for the presentation, plus 5 min for questions), except for the Young Scientists Sessions, which will be 10 min (ideally distributed using up to 7 min for the presentation plus 3 min for questions) and must be presented in English. Time scheduled for Poster flash presentations is 5 min.
Authors should provide to the organization a copy of the file of their presentations in PowerPoint format at least two hours before the session starts, although ideally should be provided the day before the presentation.

Poster presentations

Poster communication will be written in English.
Poster should have dimensions 120 cm high x 90 cm wide. Posters are displayed during the poster sessions of October 2- 3 and. They must be removed at the end of the last session, before October 4.
Author(s) must be in attendance at their poster boards during their corresponding poster session, which will be indicated in the Final Scientific Program.
Time scheduled for oral presentations of the selected posters included in the Poster Flash Sessions is 5 min, highlighting the most relevant aspects of the research presented. Authors must provide well in advance to the organizers a copy of their presentation in PowerPoint format.

Venue

Palacio de Congresos de Granada
Paseo del Violón, S/N – 18006 – GRANADA
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