



**BOOK  
OF ABSTRACTS**

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# XX Meeting of the Spanish Society of Chromatography and Related Techniques

## **SECyTA2021**

**Virtual edition, 18-19 November, 2021**

Organized by:

**SECyTA**

SOCIEDAD ESPAÑOLA DE  
CROMATOGRFIA  
Y TÉCNICAS AFINES

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# Bienvenida

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En nombre del Comité Organizador de la XX Reunión de la Sociedad Española de Cromatografía y Técnicas Afines (SECyTA 2021), os damos la bienvenida a esta edición virtual.

Después de más de un año complicado en el que la pandemia ha modificado nuestras actividades y nuestras vidas, cancelando nuestra reunión anual en 2020, somos más conscientes que nunca de nuestro papel como investigadores y de cómo la ciencia es vital en nuestra sociedad. En este panorama, nos sentimos comprometidos con nuestra labor, tanto en el desarrollo y difusión de nuevas aportaciones científicas como en la tarea de seguir formando y apoyando a los jóvenes investigadores, que son nuestro futuro y les ha tocado vivir un tiempo difícil. Especialmente pensando en nuestros jóvenes socios que siempre han tenido un papel fundamental para SECyTA, hemos organizado esta edición especial SECyTA 2021 virtual.

Esta XX Reunión de la SECyTA (49º Encuentro del Grupo de Cromatografía y Técnicas Afines) tiene lugar por primera vez virtualmente en la historia de nuestra Sociedad y nos va a permitir retomar el contacto y mantener la ilusión de volver a encontrarnos presencialmente en la próxima reunión en 2022 en Almería, organizada por el grupo de nuestra compañera Ana Agüera.

Os damos las gracias por vuestro compromiso con la Sociedad a través de vuestra participación. En esta edición virtual se han presentado 4 conferencias invitadas presentadas por especialistas relevantes en ámbitos relacionados con contaminación medioambiental, diagnóstico clínico, avances en instrumentación y tratamientos de muestra, incluyendo aplicaciones alimentarias, biomédicas o medioambientales. Igualmente el programa recoge en total 14 comunicaciones orales y 46 comunicaciones web. Este último formato sustituye al formato tradicional de poster, ya que lo hemos considerado más conveniente y dinámico para esta edición virtual.

En relación a la participación de los jóvenes socios, la acogida de esta reunión ha sido muy destacada, recogiendo en el programa 18 orales de jóvenes investigadores y 21 comunicaciones web, todas ellas presentadas a esta edición de los Premios “José Antonio García Domínguez”, patrocinados por Bruker, a los que agradecemos que una vez más sigan apoyando este premio.

Finalmente, quisiera también expresar nuestro sincero agradecimiento a las empresas que han mantenido su apoyo a la reunión en esta especial y difícil situación, manteniendo su alto compromiso con nuestra Sociedad.

Ana M. García-Campaña  
Comité Organizador

# Welcome

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On behalf of the Organizing Committee of the XX Meeting of the Spanish Society of Chromatography and Related Techniques (SECyTA 2021), it is my pleasure to welcome you at this virtual edition.

After a difficult year due to the COVID 19 situation in which our activity and life have been affected and our annual meeting was cancelled, we are more aware than ever about our work and how it affects society. In this panorama, we felt committed to both, present our scientific contributions and support young researchers, who are our future. In this sense, and especially in relation to those young researchers we have organized this edition in virtual format.

This XX Scientific Meeting of the SECyTA (49th Meeting of the Group of Chromatography and Related Techniques) that take place virtually, for the first time, on November 18-19, 2021 is a good way to get back in touch, waiting for the next meeting in 2022 in Almería, organized by the group of our colleague, Prof. Ana Agüera.

We thank you for your commitment to the Society through your participation. In this virtual edition, 4 invited lectures are presented by relevant specialists in fields related to environmental contamination, clinical diagnosis, advances in instrumentation and sample treatments, including food, biomedical or environmental applications. Likewise, the program includes a total of 32 oral communications and 46 web communications. This last format replace the traditional poster format, and we decided it I order to offer a more dynamic and efficient presentation.

Regarding the participation of young members, the reception of this meeting has been very outstanding, including in the program the presentation of 18 oral presentations and 21 web communications, all of them presented to this edition of the Awards “ José Antonio García Domínguez ”, sponsored by Bruker. We thank sincerely to Bruker the support of these awards once again.

Finally, I would like also to express our gratitude to all the companies that have supported the meeting in this special and difficult situation, maintaining a very high commitment to our Society.

Ana M. García-Campaña  
Organizing Committee



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# Program

## Thursday, November 18

### 8:45 h Opening Ceremony

Ana M. García-Campaña, Juan V. Sancho

### 9:00 h Keynote Lecture: Environmental Analysis

*Chairs: Joan Grimalt, Begoña Jiménez*

**BAREND L. VAN DROOGE**

*Trace-level analysis of molecular organic compounds in atmospheric PM by Q Exactive Orbitrap GC/MS*

### 09:45 h Oral Session 1: Environmental Analysis (I)

*Chairs: Joan Grimalt, Begoña Jiménez*

### 09:45 h O-E1: Wastewater reuse for agricultural irrigation in real crops: analytical tools and difficulties in the investigation of pharmaceutical transformation products

Patricia Plaza-Bolaños<sup>(1),(2)\*</sup>, Ana Belén Martínez-Piernas<sup>(2),(3)</sup>, Ana Agüera<sup>(1),(2)</sup>

<sup>(1)</sup> Dept. Chemistry and Physics, University of Almeria; <sup>(2)</sup> CIESOL (Center for Solar Energy Research), Joint Centre University of Almeria–CIEMAT, Almería, Spain; <sup>(3)</sup> Dept. Physical Chemistry and Analytical Chemistry, University of Jaén, Spain

### 09:55 h O-E2: Analysis of uv filters and uv stabilisers adsorbed in microplastics from canary islands beaches

Sarah Montesdeoca-Esponda<sup>\*</sup>, Sergio Santana-Viera, Zoraida Sosa-Ferrera, José Juan Santana-Rodríguez

*Instituto Universitario de Estudios Ambientales y Recursos Naturales (i-UNAT), Universidad de Las Palmas de Gran Canaria, Spain*

### 10:05 h O-E3: Ultra-high performance liquid chromatography-mass spectrometry analysis of ultraviolet filters in human nails

Laura Martín-Pozo<sup>(1)\*</sup>, María del Carmen Gómez-Regalado<sup>(1)</sup>, Samuel Cantarero-Malagón<sup>(2)</sup>, Alberto Navalón<sup>(1)</sup>, Alberto Zafra-Gómez<sup>(1,3)</sup>

<sup>(1)</sup> Analytical Chemistry and Life Sciences, Department of Analytical Chemistry, University of Granada, Spain; <sup>(2)</sup> Center for Scientific Instrumentation, University of Granada, Spain; <sup>(3)</sup> Instituto de Investigación Biosanitaria ibs, Granada, Spain

### 10:15 h Discussion

### 10:30 h Oral Session 1: Environmental Analysis (I)

*Chairs: Ana Agüera, Juan V. Sancho*

### OY-E1: Vertical distribution of volatile organic compounds and their influence on tropospheric ozone formation in Vic by using aerostatic balloons

Isabel Díez<sup>(1)</sup>, Clara Jaen<sup>(1)</sup>, Esther Marco<sup>(1)</sup>, Barend van Drooge<sup>(1)</sup>, Joan Grimalt<sup>(1)</sup>, Pilar Fernández<sup>(1)</sup>

<sup>(1)</sup> Institute of Environmental Assessment and Water Research, Barcelona, Spain

### 10:38 h OY-E2: NOVEL MULTICLASS CYANOTOXIN ANALYSIS BASED ON A DUAL CARTRIDGE SOLID-PHASE EXTRACTION SYSTEM FOLLOWED BY HYDROPHILIC INTERACCIÓN LIQUID CHROMATOGRAPHY- MASS SPECTROMETRY

M. Mar Aparicio-Muriana<sup>\*</sup>, Rocío Carmona-Molero, Francisco J. Lara, Ana M. García-Campaña, Monsalud del Olmo-Iruela

*Dept. of Analytical Chemistry, University of Granada, Spain*

### 10:46 h OY-E3: Suspect screening of micro(nano)plastics in the drinking water supply system of the Barcelona metropolitan area

Albert Vega-Herrera<sup>(1)</sup>, Marta Llorca<sup>(1)</sup>, Xavier Borrell-Díaz<sup>(1)</sup>, Katerina Savva<sup>(1)</sup>, Cristina Villanueva<sup>(2)</sup>, Esteban Abad<sup>(1)</sup>, Marinella Farré<sup>(1)\*</sup>

<sup>(1)</sup> Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Spain;

<sup>(2)</sup> Barcelona Institute for Global Health (ISGlobal), Barcelona, Spain

- 10:54 h OY-E4: Development, validation, and uncertainty assessment of a gas chromatography – electron ionization – Orbitrap mass spectrometry targeted method for POPs and PAHs in avian blood**  
Bernat Oró-Nolla<sup>(1)</sup>, Letizia Campioni<sup>(2)</sup>, Sílvia Lacorte<sup>(1)</sup>  
<sup>(1)</sup> Department of Environmental Chemistry, IDAEA-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain;  
<sup>(2)</sup> MARE - Marine and Environmental Sciences Centre, ISPA, Instituto Universitário, Lisbon, Portugal
- 11:02 h OY-E5: Investigation of antibiotics in wastewater by large-volume direct injection uhplc-ms/ms. importance of chromatography optimisation**  
Elisa Gracia-Marín<sup>\*</sup>, David Fabregat-Safont, María Ibáñez, Lubertus Bijlsma, Elena Pitarch, Félix Hernández  
 Environmental and Public Health Analytical Chemistry, Research Institute for Pesticides and Water (IUPA), University Jaume I, Castellón, Spain
- 11:10 h Discussion**
- 11:20 h Break & Exhibition**
- 12:00 h Oral Session 2: Environmental Analysis (II)**  
 Chairs: Ana Agüera, Juan V. Sancho
- 12:00 h OY-E6: Analysis of molecular compounds in organic aerosols from low-volume samples collected during meteorological balloon flights**  
Clara Jaén<sup>(1),\*</sup>, Isabel Díez<sup>(1)</sup>, Esther Marco<sup>(1)</sup>, Barend L. van Drooge<sup>(1)</sup>, Joan O. Grimalt<sup>(1)</sup>, Pilar Fernández<sup>(1)</sup>  
<sup>(1)</sup>Institute of Environmental Assessment and Water Research (IDAEA), CSIC, Barcelona, Spain
- 12:08 h OY-E7: Sweeping-micellar electrokinetic chromatography - tandem mass spectrometry as a novel approach to determine neonicotinoid and boscalid residues in pollen and honeybee samples**  
Laura Carbonell-Rozas<sup>(1),\*</sup>, Marcos Rodríguez-Vela<sup>(1)</sup>, Burkhard Horstkotte<sup>(2)</sup>, Francisco J. Lara<sup>(1)</sup>, Ana M. García-Campaña<sup>(1)</sup>  
<sup>(1)</sup> Faculty of Sciences, University of Granada, Spain; <sup>(2)</sup> Faculty of Pharmacy, Charles University, Hradec Králové, Czech Republic
- 12:16 h OY-E8: Analysis of steroid hormones sorbed on microplastics by ultrasonic assisted extraction and ultra-high performance liquid chromatography tandem mass spectrometry**  
Rayco Guedes-Alonso<sup>(1),\*</sup>, Zoraida Sosa-Ferrera<sup>(1)</sup>, José Juan Santana-Rodríguez<sup>(1)</sup>  
<sup>(1)</sup> Instituto Universitario de Estudios Ambientales y Recursos Naturales (i-UNAT), Universidad de Las Palmas de Gran Canaria, Spain
- 12:24 h Discussion**
- 12:34 h Web communications**  
 Chairs: Belén Gómara, F. Javier Santos
- 12:34 h Session A: Environmental Analysis**
- 13:04 h Session B: Clinical and Pharmaceutical Analysis/Omics Techniques**
- 13:35 h Lunch**
- 15:00 h Keynote Lecture: Clinical & Pharmaceutical Analysis**  
 Chairs: Elena González, Ana M. García-Campaña  
**JOSEP RUBERT**  
*Could gut microbial metabolites serve as a Rosetta Stone to promote gut health?*
- 15:45 h Oral Session 3: Clinical & Pharmaceutical Analysis/Omics Techniques**  
 Chairs: Elena González, Nuria Fontanals
- 15:45 h O-CF1: Tackling protein biomarkers through targeted bottom-up analysis by on-line aptamer affinity solid-phase extraction-immobilized enzyme microreactor capillary electrophoresis-mass spectrometry**  
 Hiba Salim, Roger Pero-Gascon, Estela Giménez, Fernando Benavente<sup>\*</sup>  
 Department of Chemical Engineering and Analytical Chemistry, Institute for Research on Nutrition and Food Safety (INSA·UB), University of Barcelona, Spain

- 15:55 h **O-CF2: Solute Interactions In Microemulsion Liquid Chromatography With Ionic Liquids**  
María José Ruiz-Ángel\*, Nitaben Pankajkumar-Patel, Ester Peris-García, María Celia García-Álvarez-Coque  
*Departament de Química Analítica, Universitat de València, Burjassot, Spain*
- 16:05 h **O-O1: In vitro study of the neuroprotective potential of a supercritical extract obtained from dunaliella salina microalgae**  
 Rocío Gallego, José David Sánchez-Martínez, Zully J. Suárez-Montenegro, Elena Ibáñez, Alejandro Cifuentes, Miguel Herrero, Alberto Valdés\*  
*Laboratory of Foodomics, Institute of Food Science Research (CIAL, CSIC-UAM), Madrid, Spain*
- 16:15 h **Discussion**
- 16:30 h **Oral Session 3: Clinical & Pharmaceutical Analysis/Omics Techniques**  
*Chairs: Ana M. García-Campaña, Mario Fernández*
- OY-O1: The Role of Oxidized Lipids in Fungal Mediated Diseases Using Ion Mobility-Mass Spectrometry**  
María Morán-Garrido<sup>(1),\*</sup>, Jorge Sáiz<sup>(1)</sup>, Coral Barbas<sup>(1)</sup>  
<sup>(1)</sup> CEMBIO, Facultad de Farmacia, Universidad San Pablo-CEU, Madrid, Spain
- 16:38 h **OY-O2: Differential Modulation of the Central and Peripheral Monoaminergic Neurochemicals by Deprenyl in Zebrafish Larvae**  
Marina Bellot<sup>(1),\*</sup>, Helena Bartolomé<sup>(1)</sup>, Melissa Faria<sup>(2)</sup>, Cristian Gómez-Canela<sup>(1)</sup>, Demetrio Raldúa<sup>(2)</sup>, Jordi Díaz-Ferrero<sup>(1),(2)</sup> *Department of Analytical and Applied Chemistry, School of Engineering, Institut Químic de Sarrià-Universitat Ramon Llull, Barcelona, Spain;* <sup>(2)</sup> *Institute for Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Spain*
- 16:46 h **OY-CF1: Simultaneous determination of 40 drugs of abuse and some metabolites in human urine by SPE followed by LC-MS/MS**  
Sergi Pascual-Caro<sup>(1),\*</sup>, Francesc Borrull<sup>(1)</sup>, Carme Aguilar<sup>(2)</sup>, Marta Calull<sup>(1)</sup>  
<sup>(1)</sup> *Department of Analytical Chemistry and Organic Chemistry, Universitat Rovira i Virgili, Tarragona, Spain;* <sup>(2)</sup> *Serra Hunter Professor, Department of Analytical Chemistry and Organic Chemistry, Universitat Rovira i Virgili, Tarragona, Spain*
- 16:54 h **OY-CF2: Simultaneous enantiomeric separation of licarbazepine and licarbazepine acetate by electrokinetic chromatography. Determination in pharmaceutical formulations and urine samples**  
Sandra Salido-Fortuna<sup>(1),\*</sup>, María Luisa Marina<sup>(1,2)</sup>, María Castro-Puyana<sup>(1,2)</sup>  
<sup>(1)</sup> *Universidad de Alcalá. Departamento de Química Analítica, Química Física e Ingeniería Química, Alcalá de Henares (Madrid), Spain;* <sup>(2)</sup> *Universidad de Alcalá. Instituto de Investigación Química Andrés M. del Río., Alcalá de Henares (Madrid), Spain*
- 17:02 h **Discussion**
- 17:30 h **SECYTA GENERAL ASSEMBLY**

## Friday, November 19

- 8:45 h **Keynote Lecture: New development Instrumentation & Applications**  
*Chairs: F. Javier Santos, Jordi Díaz*  
**JUAN VICENTE SANCHO LLOPIS**  
*Benefits of Collision Cross Section (CCS) data obtained by UPLC-ESI-IMS-QTOFMS and GC-APGC-IMS-QTOFMS for the identification of small molecules in screening applications*
- 09:30 h **Oral Session 4: Sample Prep. / New Develop. Instrumentation / Fundamentals/Chemometrics**  
*Chairs: F. Javier Santos, Jordi Díaz*
- 09:30 h **O-F1: DEVELOPMENT AND VALIDATION OF A METHOD FOR THE COMPREHENSIVE INSPECTION OF EXPERIMENTAL DESIGNS IN HPLC**  
María Celia García-Álvarez-Coque, José Ramón Torres-Lapasió, Adrián Gisbert-Alonso, José Antonio Navarro-Huerta  
*Departament de Química Analítica, Universitat de València, Burjassot, Spain*

- 09:40 h O-ND1: Controlled atmosphere flexible microtube plasma soft ionization source: a promising tool for the determination of small molecules by GC-MS in the field of clinical and food analysis**  
David Moreno-González<sup>(1,2),\*</sup>, Delia Castilla-Fernández<sup>(1)</sup>, Pascal Vogel<sup>(2)</sup>, Sebastian Brandt<sup>(2)</sup>, Constantinos Lazarou<sup>(3)</sup>, Odhisea Gazeli<sup>(3)</sup>, Juan F. García-Reyes<sup>(1)</sup>, Antonio Molina-Díaz<sup>(1)</sup>, Joachim Franzke<sup>(2)</sup>  
<sup>(1)</sup> Analytical Chemistry Research Group, Department of Physical and Analytical Chemistry, University of Jaén, Spain; <sup>(2)</sup> ISAS-Leibniz-Institut für Analytische Wissenschaften, Dortmund Germany; <sup>(3)</sup> FOSS Research Centre for Sustainable Energy, PV Technology, University of Cyprus
- 09:50 h O-ND2: Insights of tube plasma as a new ion source for gc-ms coupling**  
Juan F. Ayala-Cabrera<sup>(1,2),\*</sup>, Jasmin Heine<sup>(1,2)</sup>, Lidia Montero<sup>(1,2)</sup>, Sven W. Meckelmann<sup>(1,2)</sup>, Florian Uteschil<sup>(1,2)</sup>, Oliver J. Schmitz<sup>(1,2)</sup>  
<sup>(1)</sup> Applied Analytical Chemistry, University of Duisburg-Essen, Germany; <sup>(2)</sup> Teaching and Research Center for Separation, University of Duisburg-Essen, Germany
- 10:00 h Discussion**
- 10:10 h Oral Session 4: Sample Prep. / New Develop. Instrumentation / Fundamentals/Chemometrics**  
 Chairs: Juan V. Sancho, José Antonio González
- OY-S1: Combining microfluidic paper based platform and metal-organic frameworks in a single device for phenolic content assessment in fruits**  
H. Martínez-Pérez-Cejuela<sup>1,\*</sup>, Raquel B. R. Mesquita<sup>2</sup>, E.F. Simó-Alfonso<sup>1</sup>, J.M. Herrero-Martínez<sup>1</sup>, António O. S. S. Rangel<sup>2</sup>  
<sup>1</sup>Department of Analytical Chemistry, University of Valencia, Burjassot, Spain; <sup>2</sup>Universidade Católica Portuguesa, CBQF - Centro de Biotecnologia e Química Fina- Laboratório Associado, Escola Superior de Biotecnologia, Porto, Portugal
- 10:18 h OY-S2: Determination of veterinary drugs and pesticides in salmon using liquid chromatography/tandem mass spectrometry using a specific sample cleanup**  
Delia Castilla-Fernández<sup>\*</sup>, David Moreno-González, Marcos Bouza, Evaristo Ballesteros, Juan F. García-Reyes, Antonio Molina-Díaz  
 Analytical Chemistry Research Group, Department of Physical and Analytical Chemistry, University of Jaén, Spain
- 10:26 h OY-ND1: Hand-held diode laser for on-site analysis using transportable mass spectrometry**  
Ane Arrizabalaga-Larrañaga<sup>(1,2),\*</sup>, Michel W.F. Nielen<sup>(2)</sup>, Marco H. Blokland<sup>(2)</sup>  
<sup>(1)</sup> Department of Chemical Engineering and Analytical Chemistry, University of Barcelona, Spain; <sup>(2)</sup> Wageningen Food Safety Research (WFSR), Wageningen University & Research, The Netherlands
- 10:34 h OY-ND2: Exploring GC-APCI-IMS-HRMS possibilities for the screening of organic-micropollutants**  
David Izquierdo-Sandoval<sup>(1),\*</sup>, David Fabregat-Safont<sup>(1)</sup>, Leticia Lacalle-Bergeron<sup>(1)</sup>, Juan Vicente Sancho<sup>(1)</sup>, Félix Hernández<sup>(1)</sup>, Tania Portolés<sup>(1)</sup>  
<sup>(1)</sup> Environmental and Public Health Analytical Chemistry, Research Institute for Pesticides and Water (IUPA), University Jaume I, Castellón, Spain
- 10:42 h Discussion**
- 10:50 h Break & Exhibition**
- 11:20h Web communications**  
 Chairs: Nuria Fontanals, Marta Lores
- 11:20 h Session A: Sample Preparation / New Develop. Instrumentation / Fundamentals/Chemometrics**
- 11:50 h Session B: Food Analysis**
- 12:20 h Oral Session 5: Food Analysis**  
 Chairs: Belén Gómara, Mario Fernández
- 12:20 h O-FA1: Determination of intact glucosinolates in bee pollen by using ultra-high performance liquid chromatography coupled to a quadrupole time-of-flight mass detector**  
Ana María Ares<sup>(1),\*</sup>, David Sánchez<sup>(1)</sup>, Jesús Tapia<sup>(2)</sup>, Mariano Higes<sup>(3)</sup>, Amelia Virginia González Porto<sup>(3)</sup>, Raquel Martín-Hernández<sup>(3)</sup>, María Teresa Martín<sup>(1)</sup>, José Bernal<sup>(1)</sup>  
<sup>(1)</sup> I.U. CINQUIMA, GRUPO TESEA, Universidad de Valladolid, España; <sup>(2)</sup> Departamento de Estadística e Investigación Operativa, Universidad de Valladolid, España; <sup>(3)</sup> Instituto Regional de Investigación y Desarrollo Agroalimentario y Forestal de Castilla La Mancha (IRIAF), Centro de Investigación Apícola y Agroambiental, Guadalajara, España

- 12:30 h O-FA2: New solvents for bioactive compounds extraction from blueberry leaves**  
María Santos-Martín<sup>(1),\*</sup>, Ana Sayago<sup>(1,2)</sup>, Raúl González-Domínguez<sup>(1,2)</sup>, Juan Urbano<sup>(1,2)</sup>, Ángeles Fernández-Recamales<sup>(1,2)</sup>  
<sup>(1)</sup> *AgriFood Laboratory, Faculty of Experimental Sciences, University of Huelva, Spain;* <sup>(2)</sup> *International Campus of Excellence CeIA3, University of Huelva, Spain*
- 12:40 h O-FA3: Beyond the established limit: capillary gel electrophoresis of human immunoglobulin a from serum and colostrum**  
Angel Puerta<sup>(1),\*</sup>, Daniel Garcia-Lopez<sup>(1)</sup>, Paula Tejedor-Matellanes<sup>(1)</sup>, Laura Gomez-Ruiz<sup>(1)</sup>, Mercedes de Frutos<sup>(1)</sup>  
<sup>(1)</sup> *Institute of Organic Chemistry (IQOG-CSIC), Madrid, Spain*
- 12:50 h O-FA4: A label-free shotgun proteomics approach for the characterization and differentiation of quinoa seed varieties**  
Laura Pont<sup>1,\*</sup>, Rocío Galindo-Luján<sup>1</sup>, Victoria Sanz-Nebot<sup>1</sup>, Zoran Minic<sup>2</sup>, Maxim V. Berezovski<sup>2</sup>, Fernando Benavente<sup>1</sup>  
<sup>(1)</sup> *Department of Chemical Engineering and Analytical Chemistry, Institute for Research on Nutrition and Food Safety (INSA-UB), University of Barcelona, Spain;* <sup>(2)</sup> *Department of Chemistry and Biomolecular Sciences, University of Ottawa, Canada*
- 13:00 h O-FA5: Comprehensive analysis of odour-active wine volatiles by heart-cutting bidimensional gas chromatography coupled to mass spectrometry and flame ionization detection**  
O. Castejón-Musulén<sup>[1]</sup>, I. Ontañón<sup>[1]</sup>, R. Lopez<sup>[1]</sup>, V. Ferreira<sup>[1]</sup>  
<sup>[1]</sup> *Laboratorio de Análisis del Aroma y Enología (LAAE), Department of Analytical Chemistry, Universidad de Zaragoza, Instituto Agroalimentario de Aragón (IA2) (UNIZAR-CITA), Associate Unitto Instituto de las Ciencias de la Vid y del Vino (ICVV), Spain*
- 13:10 h Discussion**
- 13:25 h Oral Session 5: Food Analysis**  
*Chairs: Marta Lores, José Antonio González*
- OY-FA1: Fast non-aqueous capillary electrophoresis–mass spectrometry: an efficient alternative to determine emerging mycotoxins in food**  
María del Mar Delgado-Povedano<sup>\*</sup>, Francisco J. Lara, Emilio Borrego-Marín, Laura Gámiz-Gracia, Ana M. García-Campaña  
*Department of Analytical Chemistry, Faculty of Sciences, University of Granada, Spain*
- 13:33 h OY-FA2: Differentiation of two industrial hemp varieties by comprehensive two-dimensional liquid chromatography (lcxlc)**  
Lidia Montero<sup>(1,2),\*</sup>, Hyerin Kim, Juan F. Ayala-Cabrera<sup>(1,2)</sup>, Sven W. Meckelmann<sup>(1,2)</sup>, Oliver J. Schmitz<sup>(1,2)</sup>  
<sup>(1)</sup> *Applied Analytical Chemistry, University of Duisburg-Essen, Germany;* <sup>(2)</sup> *Teaching and Research Center for Separation, University of Duisburg-Essen, Germany*
- 13:41 h Discussion**
- 13:45 h Keynote Lecture: Sample Preparation**  
*Chairs: Juan V. Sancho, Ana M. García-Campaña*  
**VERÓNICA PINO**  
*Microextraction using novel solvents and sorbents: from green to white analytical sample preparation*
- 14:30 h Closing Ceremony & Awards**



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# KEYNOTE LECTURES

# Trace-level analysis of molecular organic compounds in atmospheric PM by Q Exactive Orbitrap GC/MS

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Air pollution is a global threat to ecosystems and affects human health. Therefore, there is a growing demand to improve the air quality. Effective action to reduce air pollution and its impacts requires a good understanding of sources, atmospheric transport, and transformation mechanisms, and the effects of these atmospheric pollutants on humans and ecosystems. Pending issues are the contributions of biomass emissions to PM and PAH (e.g. benzo[a]pyrene) in the atmosphere, as well as the formation of secondary aerosols and their influence on PM and their toxicity. Organic aerosol (OA) constitutes a highly variable fraction of PM. Understanding of the different chemical, physical, and toxicological properties of its components is important for applying effective mitigation strategies. Primary organic aerosol sources in urban areas are related to combustion engines, cooking, industrial activities, soil and road dust, among others, while biomass burning and soil dust particles are dominant in rural areas. The presence of oxidants in the atmosphere interacts with primary emitted organics in complex reactions to form oxygenated products, such as dicarboxylic acids. The oxygenated organic fraction in atmospheric PM can range from 20 to 90%, evidencing the need of understanding the role of the processes involved in secondary OA formation. Over the past decades, technological development in gas chromatography-mass spectrometry (GC-MS) resulted in instruments with high-resolution and accurate-mass (HRAM) detectors for the analysis of known and unknown chemical compounds. The technology of this system allows studying chemical compounds at trace level in environmental samples, such as atmospheric particulate matter (PM). Here we will present and discuss some of the possibilities for the application of this technique in atmospheric chemistry. [1].

## **Acknowledgements**

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## Could gut microbial metabolites serve as a Rosetta Stone to promote gut health?

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Colorectal cancer (CRC) is the second cause of death in the EU, with one million cases of CRC seen annually worldwide, and a mortality rate of 50%. In the light of these figures, and associated costs, there is an overwhelming need to prioritize and integrate primary prevention measures in existing healthcare plans. The forecasts show that the global burden of CRC is expected to increase by 60%, to over 2.2 million new cases and 1.1 million deaths by 2030, due to an aging population and western dietary patterns.

Dietary patterns, or the food we eat, are the sum of a multitude of small molecules foreign to the body. After being ingested and digested, nutrients are altered by the trillions of microorganisms that inhabit our gastrointestinal (GI) tract, shaping the chemical structures of such compounds and thus modifying the lifespan, bioavailability, and biological effects. In this context, dietary patterns modulate the gut microbiome and alter its functions by modulating the production of gut microbial metabolites (GMMs). Lastly, these GMMs are capable of regulating homeostasis and the risk of GI disease. We studied the mechanisms by which GMMs may prevent CRC and promote gut health by modelling diet-microbiome-host interactions. The first objective was to establish 3D intestinal models closely recapitulating homeostasis and carcinogenesis. Secondly, diet-gut microbiota interactions were evaluated using a GI track model. Lastly, human colon organoid and tumoroids responses to GMMs deriving from flavan-3-ols were evaluated by 3D imaging techniques and multi-omics approaches.

## Benefits of Collision Cross Section (CCS) data obtained by UPLC-ESI-IMS-QTOFMS and GC-APGC-IMS-QTOFMS for the identification of small molecules in screening applications

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Ion Mobility Spectrometry (IMS) separates ions based on their shape, mass, and  $m/z$  ratio, as well as their interactions with a “buffer” gas, making it a powerful analytical tool for investigating complex samples. Collisions occur between ions and a neutral buffer gas under an electric field, resulting in different drift times in the millisecond range. The collision cross section (CCS) of an ion is a unique IMS value and is calculated from the drift time. The chemical structure and three-dimensional conformation of a molecule influence CCS, with smaller molecules (more spherical and compact) showing smaller CCS values than the more extended ones (planar structures, extended chains, helices). With all of this chemical information stored within this value, the CCS can be used as an additional parameter in identifying a compound.

Traditionally, the detection and identification of compounds is based on the comparison of the exact mass spectra and retention time with a reference standard. However, with approaches based on conventional chromatography an additional problem arises, the isobaric components of the sample matrix can interfere with the signal of a residue or contaminant present in the sample or be confused with residues or contaminants not present in the sample, leading to false negatives or positives, respectively. However, CCS values are measured in the gas phase, away from the ion source, which means that they are not affected by the sample matrix and are consistent between instruments and between different experimental conditions. For these reasons, the use of CCS values as a fourth dimension (along with retention time, exact mass, and intensity) to identify compounds presents a great alternative for analytical chemists.

In this presentation, the benefits and disadvantages of implementing both LC-ESI-QTOFMS and GC-APCI-QTOFMS systems with IMS technology, in particular Waters Vion, in the workflow of screening and identification of residues and contaminants in complex samples will be addressed.

The main benefits of adding IMS separation to UPLC-ESI-QTOFMS and GC-APCI-QTOFMS include:

- a) Cleaner mass spectra at both low and high collision energy when aligned by IMS, similar to product ion mass spectrum (MS/MS) without the need to re-inject samples and preselect precursor ion of interest. The data can be interrogated retrospectively in the future, with good quality data for the major ions and their fragments.
- b) Possibility of solving co-eluting isobaric / isomeric compounds based on partially different ionic mobilities. Interesting for residues and contaminants, where potential isomers could be expected, as well as to discriminate conjugated isomeric metabolites.
- c) CCS values are less likely to be affected by matrix as opposed to chromatographic retention time. Therefore, the CCS values will be comparable in the same instrument family (the same ion mobility separator), which promotes the construction of empirical CCS libraries for the identification of residues and contaminants.
- d) The CCS values are related to the different shape of the ionized molecules. Therefore, CCS prediction for suspected residues or contaminants or their metabolites when their standards are lacking could be a good alternative for tentative identification along with accurate mass and fragment annotation.

# MICROEXTRACTION USING NOVEL SOLVENTS AND SORBENTS: FROM GREEN TO WHITE ANALYTICAL SAMPLE PREPARATION

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Sample preparation normally involves tedious and time-consuming steps, particularly when (i) dealing with complex samples, (ii) intending the determination of target analytes present at trace-low concentration levels, and (iii) pursuing proper compatibility with the further instrument used as detection system. In fact, it still constitutes the bottleneck of any analytical method.

The design and application of advanced functional materials with enhanced extraction and selectivity features together with safer toxicological profiles has been one of the most exploited research lines within analytical separation science in the recent years, and clearly in sample preparation. This trend, together with the utilization of microextraction and miniaturized approaches, are particularly desirable when also incorporating automation.

Among the broad variety of materials explored, our research group has paid particular attention to novel solvents, mainly ionic liquids (ILs) and their derivatives [1] – including polymeric ILs (PILs), ILs-based surfactants, and magnetic ILs (MILs), characterized by their outstanding solvation ability, high thermal and chemical stability, and impressive tunability. With respect to novel solid materials to be used as extraction sorbents, our group has mainly worked with metal-organic frameworks (MOFs) [2], crystalline materials characterized by their high surface area derived from the outstanding porosity.

The aim of this presentation is to give an overview on the use that ILs and derivatives, and MOFs, have had in our research group as novel materials for both liquid-based and solid-based microextraction strategies within analytical sample preparation, paying attention to the most recent advances together with a critical outlook on where efforts should be shifted in the field. Attention should be also paid to the real greenness of these materials, together with a consideration to their synthetic preparation. Besides, sample preparation requires a proper discussion on current trends in green analytical sample preparation, to move forward to the recent concept of white analytical chemistry-

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# ENVIRONMENTAL ANALYSIS

## O-E1

# WASTEWATER REUSE FOR AGRICULTURAL IRRIGATION IN REAL CROPS: ANALYTICAL TOOLS AND DIFFICULTIES IN THE INVESTIGATION OF PHARMACEUTICAL TRANSFORMATION PRODUCTS

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In a climate emergency context, there is a need for continuous water supplies for agricultural activities, mainly in arid and semi-arid regions, where water shortage episodes with an increasing frequency. Water reuse is a feasible and alternative source to fresh water conventional sources. Specifically, reuse of reclaimed water (RW) (wastewater treated with advanced tertiary treatments) represents an effective strategy in agreement with circular economy principles. However, chemical (and microbiological) quality of RW is currently investigated in search for contaminants of emerging concern (CECs) and new transformation products (TPs) that may pose a risk for health through the consumption of the final vegetable products and/or that could be harmful to the environment due to their continuous release through agricultural systems. Investigation of new TPs in environmental compartments is essential to detect relevant compounds that can show similar or higher toxicity than parent compounds.

This work investigates the occurrence of pharmaceutical TPs in real agricultural systems (water, soil, and plant leaves and tomato fruits) that have been irrigated with reclaimed water (tertiary treatment: chlorination) for more than ten years. A prioritization list containing 20 parent pharmaceuticals, previously identified in the agricultural area under study [1, 2], was defined based on concentration and detection frequency in the water-soil-plant nexus. Next, a suspect screening strategy was applied by LC-QTOF-MS in search for potential TPs of the selected compounds. A TP list was built based on TPs reported in literature and potential TP structures proposed by *in silico* tools (EAWAG-BBD Pathway Prediction System). The final TP list contained 262 TPs. Difficulties in the tentative identification of the TPs included the lack of high-quality MS/MS spectra and the lack of available commercial standards to confirm the proposed structures. Up to 18 TPs could be tentatively identified and 7 of them were confirmed with commercial standards. Finally, an estimation of the toxicity of the identified TPs was carried out using QSAR models.

### Acknowledgements

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## O-E2

# ANALYSIS OF UV FILTERS AND UV STABILISERS ADSORBED IN MICROPLASTICS FROM CANARY ISLANDS BEACHES

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The presence of plastic and microplastic residues in the ocean is an environmental problem that has gained great attention last years. They reach to the environment from the fragmentation of larger plastics, microparticles coming from cosmetic products, synthetic fibers generated during washing laundry and resin pellets from the plastic industry lost during production [1]

Apart from the damage that microplastic ingestion can exert in marine organisms, the pollutants that they can contain may involve another risk associated to these anthropogenic materials. Many organic compounds can be adsorbed onto the surface of microplastics because of their hydrophilic behavior; for example, ingredients added to personal care products such as sunscreens. Therefore, microplastics can act as vectors of pollution [2-4].

A methodology based on ultrasound-assisted extraction and ultrahigh-performance liquid chromatography with tandem mass spectrometry detection was developed and applied to determine 12 UV filters and UV stabilisers in microplastics. The analyses of samples taken in 13 sand beaches from the Canary Islands revealed the presence of 10 of the target compounds at concentrations between 1 and 4031 ng·g<sup>-1</sup>. The UV filter octocrylene highlighted for its detection frequency (85% of the samples). Although the source of the microplastic could be far away and be transported by the Canary Current, the detection of high concentrations of these compounds in coast of Canary Islands could be related with its great touristic pressure.

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## O-E3

# ULTRA-HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY ANALYSIS OF ULTRAVIOLET FILTERS IN HUMAN NAILS

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Ultraviolet filters (UV-filters) are a family of organic compounds that absorb and reflect UVA and UVB radiation from the sun. They are widely used in personal care products and sunscreens, and in products such as plastics, adhesives, toys, or furniture finishes. The present work develops and validates a new method for the determination of eight UV-filters (BP-1, BP-2, BP-3, BP-6, BP-8, 4-OH-BP, THB, AVB) in human nail samples. Nails are easy to collect and handle, and are useful markers for assessing cumulative and continuous exposure to harmful chemicals.

The proposed treatment of nail samples is based on microwave assisted digestion/extraction (MAE) using a methanolic solution of o-phosphoric acid (0.05 mol L<sup>-1</sup>) followed by determination using ultra-high performance liquid chromatography-mass spectrometry (UHPLC-MS/MS) in multiple reaction monitoring mode. The compounds were separated in less of 10 min. The digestion procedure was optimized using multivariate strategies. For validation purposes, a matrix-matched calibration with a pig hoof matrix was performed. A study of accuracy with spiked blank samples was also conducted. The calculated detection limits varied between 0.2 and 1.5 ng g<sup>-1</sup>, and quantification limits between 1.0 and 5.0 ng g<sup>-1</sup>. The trueness of the method was an estimation of the recovery, which was between 90.2% and 112.2%; with an estimated precision (relative standard deviation, % RSD) lower than 12.3% for all UV-filters.

The method was satisfactorily applied to nail samples obtained from 22 volunteers (male and female). The results showed that all samples tested positive for at least two benzophenone UV-filters, with BP-1 and BP-3 being the most predominant. The high frequencies and concentrations found are indicative of a high exposure and long-term bioaccumulation of these compounds, with the consequent health risks they could pose as endocrine disruptors.

### Acknowledgements

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## OY-E1

### Vertical distribution of volatile organic compounds and their influence on tropospheric ozone formation in Vic by using aerostatic balloons

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In order to execute effective pollution control measures it is essential to know and understand the mechanisms of formation of air pollutants and their characteristics. Besides direct emissions of contaminants toward the atmosphere, air pollution is related to changes in weather conditions. Atmospheric thermal inversion episodes imply stagnant conditions that restrict the dispersion of atmospheric pollutants and fostering the transformation of chemical compounds through photooxidation that is related to Secondary Organic Aerosol (SOA) and ozone (O<sub>3</sub>) formation. In central Catalonia, the region of Plana de Vic undergoes frequently thermal inversion conditions, leading to accumulation of air pollution in a thin air layer near the surface. On the other hand, this area shows one of the highest summer concentrations of ozone of the Iberian Peninsula. Volatile organic compounds (VOCs) are a major group of air pollutants known to be precursors of ground-level tropospheric O<sub>3</sub> and SOA formation. The aim of this work is the study of the chemical composition of VOCs and O<sub>3</sub> within and above the thermal inversion layer. The vertical analysis was performed by using aerostatic balloons fitted with active sampling pumps and adsorbent cartridges (fig. 1). Two sampling campaigns were performed during winter (15th-17th March, 2021) and summer (29th June – 1st July, 2021) periods to assess the seasonal variations of VOCs on molecular level including both biogenic (isoprene and monoterpenes) and anthropogenic ones (alkanes, alkenes, aromatic hydrocarbons and oxygenated compounds). The chemical analysis was carried out by thermal desorption-gas chromatography mass spectrometry (TD-GC-MS) and high-performance liquid chromatography (HPLC) techniques



**Figure1.** Aerostatic balloon equipped with active samplers.

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## OY-E2

# NOVEL MULTICLASS CYANOTOXIN ANALYSIS BASED ON A DUAL CARTRIDGE SOLID-PHASE EXTRACTION SYSTEM FOLLOWED BY HYDROPHILIC INTERACCION LIQUID CHROMATOGRAPHY- MASS SPECTROMETRY

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Cyanotoxins are toxic secondary metabolites produced by blue-green algae. Their presence in all kinds of water bodies such as sea and fresh water sources, may be harmful to surrounding flora, fauna and humans due to the consumption of contaminated drinking water and even skin exposure during recreational activities. Cyanotoxins present a great variety of structures and physicochemical properties [1], hence for risk assessment and studies on occurrence, the development of reliable and sensitive analytical approaches able to cover a wide range of cyanotoxins is highly challenging [2]. This work describes the development of a HILIC-MS/MS multiclass method for the simultaneous determination of eight cyanotoxins in reservoir water samples. They belong to three different classes according to their chemical structure: cyclic peptides (microcystin-LR, microcystin-RR and nodularin), alkaloids (cylindrospermopsin, anatoxin-a) and three non-protein amino acids isomers such as  $\beta$ -methylamino-L-alanine, 2,4-diaminobutyric acid and N-(2-aminoethyl)glycine). A SeQuant ZIC-HILIC column was employed to achieve the chromatographic separation in less than 12 min using water and acetonitrile, both acidified with 0.3% of formic acid, as mobile phase. Previously, a novel sample treatment based on a tandem solid-phase extraction (SPE) system using mixed-mode cation exchange (MCX) and Strata-X cartridges was investigated to extract and preconcentrate this chemically diverse group of cyanotoxins. The Strata-X cartridge, which was configured first in the line of sample flow, retained the low polar compounds while the MCX cartridge, which was at the bottom of the dual system, mainly retained the non-protein amino acids. For analyte elution it was required to reverse the order of the cartridges. Method validation was carried out in terms of linearity, limit of detection (LOD) and quantification (LOQ), recoveries, matrix effect and precision in terms of repeatability and intermediate precision. This work represents the first analytical method for the simultaneous analysis of these multiclass cyanotoxins in reservoir water samples, achieving LOQs in the very low range of 7 – 100 ng·L<sup>-1</sup>. Recoveries obtained at the LOQ concentration levels ranged from 70.9 to 101.0% for all compounds except for BMAA and DAB in freshwater samples where ionic strength was higher.

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## OY-E3

### Suspect screening of micro(nano)plastics in the drinking water supply system of the Barcelona metropolitan area

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This work reports the micro and nanoplastics (MNPLs) with size ranges from 0.7 to 20 µm found in tap water samples of the Barcelona metropolitan area (BMA) collected during a sampling campaign carried out in September and October 2020. Tap water samples were collected from home pipes of volunteers distributed in the zip codes of the BMA.

To identify and quantify the polymers in the samples, a suspected screening validated method based on high-performance liquid chromatography coupled to high-resolution mass spectrometry (HPLC-HRMS) using an advanced polymer chromatography column (Acquity APC XT45 1.7 µm) and atmospheric pressure photoionization (APPI) source under negative and positive conditions was used taking into account a previous method developed and validated in our research group for MNPLs in seawater compartments [1]. The acquisition was performed in full scan mode, and the subsequent tentative identification was based on the Kendrick Mass Defect analysis (KMD).

The main results of the samples showed that polyethylene (PE), polypropylene (PP), polyisoprene (PI), polystyrene (PS), polybutadiene (PBD), polyamide (PA) and polydimethylsiloxanes (PDMS) were most commonly found. In particular, PE, PP and PA, while the polymers found at high concentrations were PI reaching 39 µg/L and PBD reaching 27 µg/L.

A principal component analysis (PCA) was performed to assess if there are significant differences (confidence level 95%) between districts. Despite the fact that significant differences were not found among the studied area, there is a trend indicating that the samples collected at the west part of BMA presented a higher number of polymers and at higher concentrations.

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## OY-E4

# Development, validation, and uncertainty assessment of a gas chromatography – electron ionization – Orbitrap mass spectrometry targeted method for POPs and PAHs in avian blood

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Organic pollution is known to have a direct impact on wildlife and especially on threatened avian species (Alharbi et al., 2018). We base this study on the optimization of a targeted multiresidue analysis to determine 54 persistent organic pollutants (POPs) including organochlorinated pesticides (OCPs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and polycyclic aromatic hydrocarbons (PAHs) in blood of Bermuda petrel (*Pterodroma cahow*), an endemic and endangered species from Bermuda Islands considered extinct for more than 300 years with 134 mature adult mature pairs nowadays thanks to recovery programs (Madeiros et al., 2012). Because of the high level of protection of this species, very small volume of blood can be collected and contaminants are expected to be found at low concentrations. For those reasons, the extraction conditions with hexane, ethyl acetate and dichloromethane and the clean-up procedures were optimized to obtain high efficiency and sensitivity. Gas chromatography (GC) coupled to Orbitrap high resolution mass spectrometry (GC-Orbitrap-HRMS) has been used to determine target compounds because of its tremendous potential for the low-level analysis of contaminants in biological samples (Mol. Et al., 2016). To validate the developed method, we have estimated the uncertainty of the extraction and analytical procedures using blood samples spiked at very low concentration (2 ng/mL) and the precision (us) and the bias (ub) were calculated for 3 extraction methods, to finally estimate the combined uncertainty (u) and the expanded uncertainty (U). Finally, *Pterodroma cahow* blood samples (n=5) were analysed and 4,4'-DDE, PCBs, phenanthrene and anthracene were detected at concentrations ranging between 0.36 and 28.3 ng/mL. The method herein proposed permits to analyse very low blood volumes respecting the ethical principles of less-invasive sampling, fundamental when studying threatened wildlife bird species.

### Acknowledgements

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## OY-E5

# INVESTIGATION OF ANTIBIOTICS IN WASTEWATER BY LARGE-VOLUME DIRECT INJECTION UHPLC-MS/MS. IMPORTANCE OF CHROMATOGRAPHY OPTIMISATION

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The presence of pharmaceutically active substances in aquatic ecosystems is of great interest due to their potential negative effects on the quality of water and living organisms. Among pharmaceuticals, antibiotics are of special concern as they may promote bacterial resistance, even at low concentrations, through prolonged exposure [1].

In this work, a multiresidue method to determine 16 antibiotics in effluent and influent wastewater has been developed and validated. The list of compounds includes 3 penicillins (amoxicillin, ampicillin and cloxacillin), 5 macrolides (azithromycin, clarithromycin, clindamycin, erythromycin and roxithromycin), 4 quinolones (ciprofloxacin, levofloxacin, moxifloxacin, norfloxacin), one tetracycline (doxycycline) as well as sulfamethoxazole, trimethoprim, and metronidazole. The compounds were selected based on their highest use in the Valencian Region, four of which are included in the EU Watch List 2020 [2].

The procedure is based on liquid chromatography/electrospray tandem mass spectrometry (UHPLC-ESI-MS/MS). Due to the high polarity differences between the studied compounds, which hampers their simultaneous preconcentration by solid phase extraction, large-volume direct injection was used to achieve the required sensitivity. Moreover, the optimization of both chromatography and mass conditions resulted crucial.

The method was validated at 100, 500 and 5000 ng/L, in different influent and effluent wastewater samples. Due to the high complexity of this matrix, and the high variability expected among them, the use of isotopically-labeled internal standards was required for obtaining satisfactory results.

Finally, the developed methodology was applied to the analysis of samples collected from different wastewater treatment plants located in the area of study. Data obtained illustrates the wide use and impact of antibiotics in this region.

### Acknowledgements

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## OY-E6

# ANALYSIS OF MOLECULAR COMPOUNDS IN ORGANIC AEROSOLS FROM LOW-VOLUME SAMPLES COLLECTED DURING METEOROLOGICAL BALLOON FLIGHTS

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Atmospheric temperature inversion episodes often involve precautionary health warnings as they encompass strong increases of atmospheric pollutant concentrations. Restricted dispersion of organic compounds and photooxidation in the upper air layers lead to qualitative and quantitative changes of atmospheric aerosols that are largely unknown. Understanding the main changes in composition of these compounds at molecular level will help to define the best strategies to deal with the health risks of the temperature inversion episodes.



Figure 1. BC and PM sampling with a captive balloon.

The present study is devoted to the analysis of the vertical distribution of particle-associated organic pollutants and Black Carbon (BC) which was performed with the use of captive balloons equipped with particulate matter (PM) samplers and BC monitors. Online data was collected and off-line data was obtained from filter analysis and high-resolution accurate mass GC-MS.

The organic pollutants generated under several types of temperature inversions in urban and rural environments in different seasons were studied. One of these environments is located in the area of Osona (Catalonia, Spain) where the highest winter benzo[a]pyrene concentrations among those recorded in the Iberian Peninsula have been observed. The temperature inversions in the plain systems and associated atmospheric transport of organic pollutants, prior and after respective photooxidation, have been studied.

The particle-associated pollutants involve polycyclic aromatic hydrocarbons (PAHs), saccharides, hopanes, phthalates and SOA-compounds and some of them were used as tracers to identify the contribution of emission sources and secondary formation to PM.

### Acknowledgements

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## OY-E7

# Sweeping-micellar electrokinetic chromatography - tandem mass spectrometry as a novel approach to determine neonicotinoid and boscalid residues in pollen and honeybee samples

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In this work, we propose for the first time an electrophoretic method based on micellar electrokinetic chromatography tandem mass spectrometry (MEKC-MS/MS) for the simultaneous determination of nine neonicotinoids (NNIs) together with the fungicide boscalid in pollen and honeybee samples. The use of these pesticides has been related with the colony collapse disorder (CCD) produced in honeybees due to their toxic effects to beneficial and non-target insects such as pollinators [1]. The European Food Safety Authority (EFSA) has restricted their uses to protect them, and maximum residue limits (MRLs) have been set in a high number of food commodities in order to protect human health [2].

The electrophoretic separation was performed using ammonium perfluorooctanoate (APFO, 50 mM, pH 9) as both volatile surfactant and electrophoretic buffer compatible with MS detection. A stacking strategy to achieve an on-line pre-concentration of the target compounds, known as sweeping, was carried out to improve peak efficiency and sensitivity. Furthermore, a scaled-down QuEChERS was developed as sample treatment, involving a lower organic solvent consumption, using Z-Sep+ as dispersive sorbent in the clean-up step. A triple quadrupole mass spectrometer was operating in positive ion electrospray mode (ESI+) under multiple reaction monitoring (MRM). The main parameters affecting MS/MS detection as well as the composition of the sheath-liquid (ethanol/ultrapure water/formic acid, 50:45.5:0.5 v/v/v) and other electrospray variables were optimized to achieve satisfactory sensitivity and reproducibility. Procedural calibration curves were established in pollen and honeybee samples with LOQs below 11.6  $\mu\text{g kg}^{-1}$  and 12.5  $\mu\text{g kg}^{-1}$ , respectively. Precision, (% RSD), lower than 15.2 % and recoveries higher than 70 % were obtained in both samples. Two positive samples of pollen were positives in imidacloprid and thiamethoxam. Imidacloprid was also found in a sample of dead honeybees. The proposed method is an environmentally friendly, efficient, sensitive and useful alternative to the commonly used LC methods for the determination of NNIs and boscalid in pollen and honeybee samples.

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## OY-E8

# ANALYSIS OF STEROID HORMONES SORBED ON MIROPLASTICS BY ULTRASONIC ASSISTED EXTRACTION AND ULTRA-HIGH PERFORMANCE LIQUID CHROMATOGRAPHY TANDEM MASS SPECTROMETRY

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Microplastics (MPs) are plastic particles with a size diameter < 5 mm and they have become an important environmental threat because their persistence and toxic effects on marine and aquatic organisms [1]. In addition to the harmful effects produced by microplastics themselves, they can become vectors for other pollutants, such as emerging pollutants (EPs), that may be adsorbed on their surface. Steroid hormones are a group of these emerging pollutants which to the knowledge of the authors have not been studied in MPs. Steroid hormones have been detected in marine waters at concentrations of ng·L<sup>-1</sup>, which are enough to harm exposed biota [2]. Steroid hormones exhibit octanol-water partition coefficients over 2, which indicates that they are likely to adsorb on organic matrices, such as the sediment or solid particles present in STP effluents like MPs.

In this regard, it is necessary to develop extraction procedures which permits to extract pollutants adsorbed on MPs. Maceration or soaking procedures involve large organic solvent volumes and long extraction times [3] therefore, ultrasonic-assisted extraction (UAE) could be a greener alternative to extract EPs in comparison with these extraction methods. The combination of UAE to ultra-high performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS) results in a sensitive and selective analytical methodology to determine the concentrations at which the adsorbed EPs are found on MPs.

In this work, the optimization of a UAE-UHPLC-MS/MS to determine 13 steroid hormone residues absorbed on MPs was developed. To get the optimum extraction conditions, a factorial experimental design was followed to evaluate the effect of the variables involved in the process. The optimized method was successfully applied to samples of microplastic fragments and plastic pellets taken in beaches from Canary Islands.

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## WC-E1

# CONTINUOUS MONITORING OF VOCs THROUGH SENSORIZATION. AUTOMATIC SAMPLING DURING ODOUR/NUISANCE EPISODIC EVENTS

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Volatile organic compounds (VOCs) are a highly diverse class of chemical contaminants and between 50 and 300 of them may be found in ambient air [1]. In urbanized areas, VOCs are emitted in a relevant way from industrial activities, as well as from vehicle-related and combustion sources [2]. VOCs in outdoor air can be detected in a broad range of concentrations (from ppt to ppb) [3], usually varying seasonally [2]. The presence of VOCs at relatively high concentrations has been related to poor air quality, discomfort and odorous nuisances [4]. Additionally, they can have negative health effects to the human organism [5].

Hence, in locations where recurrent sporadic situations of high VOCs levels take place, episodic samples' evaluation is necessary instead of 24 hour or longer sampling period's evaluations. The use of commercially available metal oxide semiconductor gas sensors for a continuous monitoring (obtaining relative values) of VOCs concentrations in outdoor air is an interesting and innovative technology. Additionally, the use of these sensors for the activation of a VOCs sampler when episodic events of nuisance/odorous annoyance occur has been successfully evaluated using TD-GC/MS analysis. The sensor activation is induced by higher VOCs concentrations from a wide number of VOC chemical families [6].

Two sensor stations, developed at our laboratory and provided with sampling pumps, were located in the municipality of Santa Margarida i els Monjos (Catalunya, Spain) in January 2021. The stations started recording data continuously from two different types of VOCs sensors, temperature, relative humidity and pressure in 1.5-minute periods. Automatic VOCs sampling was conducted, using multi-sorbent bed tubes, during the months of June-July when the sensors electronic values exceeded a set point value (established in the value of the typical baseline for each location). Samples were analyzed through TD-GC/MS. TVOC concentrations in episode samples ranged between 77-673 and 12-158  $\mu\text{g}/\text{m}^3$  in Site 1 and Site 2, respectively. Although TCOV concentrations were not high in all cases, relevant concentrations of chloroform were observed, especially in Site 1, with concentrations ranging from 19-160  $\mu\text{g}/\text{m}^3$ .

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**WC-E2**  
**DETERMINATION OF ACARICIDE RESIDUES IN BEESWAX BY USING GAS  
CHROMATOGRAPHY-MASS SPECTROMETRY**

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In recent years, many European and North American countries have reported severe losses in honey bee populations. Beekeepers employ acaricides to control various types of mites whose effectiveness is decreasing due in large part to resistance phenomena. This situation causes that dose higher than those recommended are frequently applied, which implies a high probability of residues appearing in the different products of the hive, mainly pollen and beeswax. This present work is based on increasing knowledge about the presence of the most frequently detected pesticides in beeswax by determining their content in beeswax sheets (natural, purified and decontaminated), usually used by Spanish beekeepers. For that reason, a novel method is proposed to determine the residues of seven acaricides (atrazine, chlorpyrifos, chlorfenvinphos, alpha-endosulfan, bromopropylate, coumaphos, tau-fluvalinate) in beeswax by means of gas chromatography coupled to mass spectrometry.

An efficient sample treatment (recoveries between 90% and 108%) is proposed, involving solvent extraction with 1% acetic acid in acetonitrile mixture followed by dispersive solid-phase extraction (enhanced matrix removal lipid) and a polishing step. An evaluation was made of the analytical performance of the proposed method. Chromatographic conditions were also optimized using a non-polar phenyl arylene polymer column with a temperature program that allows the separation of all compounds in less than 20 min. It was shown to be selective, linear from a limit of quantification to 5000 µg/kg, precise (relative standard deviation values were below 6%), and with a good sensitivity (limit of quantification ranging from 5 to 10 µg/kg). Finally, results showed that a large majority of the sheets analyzed (>90%) contained residues of at least one of these compounds. Coumaphos and tau-fluvalinate residues were the most common, with chlorpyrifos and chlorfenvinphos detected to a lesser extent.

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## WC-E3

### ASSESSING THE ORIGIN OF LIPID BIOMARKERS IN VOLCANIC CAVE ENVIRONMENTS

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Lipid biomarkers are stable organic biosignatures, at geological time scales, that are frequently used as paleoenvironmental proxies [1,2]. Although these biomarkers are commonly reported in marine and terrestrial environments, the source of lipids in subterranean ambients are poorly understood [3]. They can be the result of subsurface microbial activity or vegetation biomass from overlying surface soils [2]. The goal of this work was the assessment of lipid molecules preserved in silicious speleothems in different lava tubes from Lanzarote Island (Spain). The presence of lipid biomarkers was evaluated in 6 speleothem samples from 5 different volcanic caves. *n*-Alkane homologous series was directly analyzed by analytical pyrolysis (Py-GC/MS), monitoring the *m/z* 85 single ion. Fatty Acid Methyl Esters (FAMES) characterization was performed by gas chromatography (GC/MS) techniques after the acidification, derivatization, and purification of the extractable organic matter (EOM). Bulk isotopic signature of light elements ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) was measured by an isotope ratio mass spectrometer coupled to an elemental analyzer (EA/IRMS).

The characteristic distribution of *n*-alkanes, with a prevalence of short C chain length ( $<C_{21}$ ), indicates a microbial origin [2]. The non-clear preference for odd or even C chain length may also suggest bacteria communities as the main lipid sources. Some speleothem samples displayed a relatively high contribution of long C chain *n*-alkanes. This trend suggests the contribution of surface plant biomass since these compounds have been reported as plant biomarkers [1]. On the other hand, FAMES distribution was predominantly dominated by short ( $C_{<20}$ ) even-over-odd C chain lengths, with a maximum at  $C_{16}$ . This pattern was observed in bacterial communities [2,3]. In addition, some samples showed long C chain FAMES ( $C_{>20}$ ), which may confirm a relative significant contribution of aboveground fresh vegetation material [1]. The contribution of surface biomass is supported by the significant lowest  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  values, in range of  $C_3$  plants [4]. The molecular signatures of lipid-like compounds can be helpful for the search of potential traces of present and past live and their environmental adaptation.

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## WC-E4

# CHARACTERIZATION OF PACKAGING MATERIALS AND PROTECTION OF CULTURAL ASSETS BY FTIRM AND SEM AND CHROMATOGRAPHIC DETERMINATION OF VOCs IN THE MATERIALS AND IN SPACES INTENDED FOR THE CONSERVATION OF HERITAGE.

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There is a growing concern in the field of conservation of cultural heritage to prevent and avoid potential damage on cultural property that is part of the collection of a museum. This property can be either directly exhibited, or stored in the museum's reserves. Among several actions that can be taken to minimize the risks, the study of both the materials used for protection and packaging of cultural property and of the spaces intended for its exhibition and storage are fundamental.

The objectives of this study are the characterization and determination of volatile organic compounds (VOCs) in 17 materials used for protection and packaging of Cultural Property, and the determination of VOCs in the air of two spaces intended for the exhibition and storage of Cultural Property.

The 17 materials have been characterized by Fourier transform infrared microspectroscopy (FTIRM) and Scanning Electron Microscopy (SEM) techniques. Determination of VOCs has been carried out by headspace coupled to gas chromatography with detection by flame ionization and mass spectrometry (HS-GC-FID/MS). Gases emitted from the materials when heated for 5 h at 120 °C are studied by these techniques. The procedure followed is based on the Volkswagen PV 3341 test method.

Determination of VOCs in spaces intended for the exhibition and storage of cultural property has been carried out by HS-GC-MS and GC-MS. VOCs are captured in passive samplers with different kinds of carbon as adsorbent material and are kept in contact with air for 27 days. Adsorbed compounds are desorbed with dimethylacetamide (DMA), and the resulting liquid extract is analyzed by HS-GC-MS and by direct injection in GC-MS to ensure detection of a wide range of volatilities.

Application of these chromatographic methods to the samples of materials has allowed to calculate the amount of VOCs emitted by the 17 materials and to identify 23 different compounds. In the other hand, analysis of the passive samplers has allowed to identify 75 different compounds in the two sampling zones.

### References

PV3341 Standard, Emission of Organic Compounds/Total Emissions/VOC

## WC-E5

# STUDY OF VOLATILE ORGANIC COMPOUNDS (ALDEHIDES) IN THE AIR OF SPACES DESIGNATED FOR THE CONSERVATION AND EXHIBITION OF ASSETS OF THE CULTURAL HERITAGE OF THE MNAC

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In the field of heritage conservation, there is a growing interest in preventing and avoiding potential damage to cultural assets that are part of a museum's collection, which includes both the exhibited assets and those stored in its reserves. Among the different actions that can be taken to minimize risks, the study of volatile organic compounds (VOCs) present in the air of the spaces intended for the exhibition and storage of the works of art is essential. Among the VOCs, formaldehyde, acetaldehyde and organic acids are of special interest. The objective of this work is to identify and quantify the aldehydes, present in the air of 3 spaces of the *Museu Nacional d'Art de Catalunya* (MNAC): a showcase and two reserves.

The analytes are captured in passive samplers with dinitrophenylhydrazine (DNPH) that are kept in contact with air for 7 days. The analytes are desorbed with acetonitrile and the extract obtained is analyzed by HPLC-DAD and UPLC-MS / QTOF. The limits of quantification for formaldehyde and acetaldehyde (0.1 and 0.2 ppbv) allow to measure the minimum values established by *The Getty Conservation Institute* [1].

The air in the reserves has a content of formaldehyde (8.1-12.2 ppbv) and acetaldehyde (0.9-1.1 ppbv), notably lower than that of the showcase (84.3 ppbv and 8.2 ppbv). In the reserves, the concentration of formaldehyde in the air is suitable for museum collections in general (0.1-20 ppbv), while in the showcase the value obtained indicates that actions are required to reduce its presence (16-120 ppbv). In the reserves and the showcase, the acetaldehyde concentration is adequate for general collection storage.

In the showcase, four linear aliphatic aldehydes (propanal, butanal, pentanal, and hexanal) are also detected. These compounds have been identified by coincidence of retention times and have been confirmed by their absorbance ratio at two wavelengths (270 nm, 360 nm). Their concentrations are less than 1.5 ppbv, except for hexanal (17 ppbv). Finally, the UPLC- MS / QTOF technique has made it possible to confirm the presence of the 6 linear aliphatic aldehydes in the showcase, and to assign an empirical formula to 7 new compounds.

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## WC-E6

### ASSESSMENT OF POPs IN TWO DISTINCT POPULATIONS OF SPERM WHALES

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In the last years, the scientific community drew attention to the hazard that some persistent organic pollutants (POPs) continue to represent to human health and wildlife [1]. Very high and stable levels have been reported in many regions such as the Mediterranean Sea, at the same time that some studies suggested a potential role of these substances in the decline of some cetacean populations [2]. As widely known, lipophilic POPs can biomagnify along food webs reaching high levels in some cetacean species and causing several adverse health effects. Therefore, marine mammals represent a useful tool for pollution biomonitoring.

In this work we compare levels of PCBs, DDTs and HCB analyzed by GC-ECD, in subcutaneous blubber of two genetically distinct sperm whale populations (Canary Islands and Mediterranean Sea populations) [3]. Additionally, we discuss levels of PBDEs, dl-PCBs and PCDD/Fs reported by a more recent study on Mediterranean sperm whales, quantified by the isotopic dilution technique by GC-HRMS [4]. All specimens analyzed in these studies were stranded between 2006 and 2016.

The Mediterranean Sea shows the highest levels of POPs, confirming this area as a PCBs' "hot spot" for marine mammals. Both areas show the same relative abundance of target contaminants (DDTs>PCBs>HCB) and no recent inputs of DDTs. 86% of the study animals exceeded the toxicity threshold for PCBs and all sperm whales surpassed the threshold value for immunosuppression. The high contribution of dl-PCBs to total WHO-TEQs (63%) shows the toxicological relevance of these legacy contaminants, which despite having been banned for decades still represent a substantial contribution to the global contamination. These results emphasize the importance of continuous monitoring of POPs in cetaceans, above all in populations at high risk of extinction and inhabiting industrialized regions, as well as the use of reliable analytical methods.

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**WC-E7**  
**NON-TARGET ANALYSIS OF POLLUTANTS IN CONTAMINATED SEDIMENTS BY  
COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY–TIME-OF-FLIGHT  
MASS SPECTROMETRY**

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The amount and number of synthetic chemicals in use has significantly increased over the last decades. Many of these compounds have been demonstrated to be able to reach and distribute in the environment [1]. National and international environmental monitoring programs are constantly updated to include new chemicals with persistent, bioaccumulative and toxic (PBT) characteristics. However, a large number of chemical substances in wide commercial use are still not measured in environmental samples on a regular basis, and their environmental fate remains unknown. The increasing awareness of our surrounding environment as a source of human exposure to a large number of known and unknown chemicals and the adoption of the exposome concept has led to an interest in holistic approaches that allow a more comprehensive assessment of contaminants in the environmental matrices. Despite the inherent complexity of these types of approaches, from an analytical point of view, the technological and instrumental advances of the last decades have enabled a significant progress in this research field. Such an increasingly holistic characterization typically relies on the enhanced chromatographic [2] and/or mass spectral resolution [3] of the instrumental techniques selected for final analytical characterization of the investigated samples.

This study evaluates the feasibility of comprehensive two-dimensional gas chromatography combined with time-of-flight mass spectrometry (GC×GC–ToF MS) for the suspect and non-target screening (NTS) of organic compounds in complex environmental matrices. In particular, the enhanced separation power and characterization capabilities of GC×GC–ToF MS have been used for the identification and annotation of organic pollutants of a widely divergent chemical nature in sediments collected in a contaminated area close to Madrid. Samples were collected in spring 2017, after the explosion of the distillation reactor of a company dedicated to solvent recovery and recycling of industrial wastes and the subsequent uncontrolled fire of the installation.

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## WC-E8

# USING COLLISION-CROSS SECTION FOR FILTERING HIGH-RESOLUTION MASS SPECTROMETRY DATA DURING TARGET AND SUSPECT WIDE-SCOPE SCREENING: APPLICATION TO AMAZON RIVER SAMPLES

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High-resolution mass spectrometry equipped with ion mobility separation (IMS-HRMS) instruments have become highly popular in the last years. Among its benefits, the most important are the collision-cross section (CCS) values of the compounds of interest, which can be used as a chromatographic-independent identification parameter, as well as the alignment of fragment ions with the corresponding precursor based on mobility data when working with data independent acquisition modes [1]. Nevertheless, IMS-HRMS data processing can be highly time-consuming, especially for wide-scope screening analyses.

In our work, we have proposed an analytical workflow for target and suspect liquid chromatography-IMS-HRMS screening based on data filtering using different identification parameters. For target screening, chromatographic retention time, mass accuracy and empirical CCS values were used. Regarding suspect screening, different steps were proposed to reduce the number of potential detections in which fragmentation should be evaluated for their tentative identification. These steps included an initial accurate-mass filtering and removal of peaks present in blank samples, followed by predicted CCS using Artificial Neural Networks [2].

The analytical workflow was tested for the analysis of 40 surface water samples collected along the Amazon River and its tributaries crossing four important urban areas of the Brazilian Amazon (Manaus, Santarém, Macapá, Belém). More than 900 compounds were investigated, and up to 51 drugs and metabolites were identified. The highest prevalence was found in streams crossing the urban areas of Manaus, Macapá and Belém. Most compounds identified in areas with significant urban impact belonged to the analgesics and antihypertensive categories, followed by stimulants and antibiotics. Compounds such as caffeine, cocaine and its metabolite benzoylecgonine, and cotinine (the metabolite of nicotine), were also detected in areas with relatively low anthropogenic impact and showed the highest total prevalence.

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## WC-E9

# OCCURRENCE OF PHARMACEUTICAL RESIDUES IN A CONVENTIONAL WASTEWATER TREATMENT PLANT IN THE PROVINCE OF CASTELLÓN (SPAIN)

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The presence of pharmaceutical residues in the aqueous environment has become a topic of great interest due to the effects and risks that they pose to the ecosystem. Furthermore, it has been demonstrated that the main source of pharmaceutical contamination in surface water comes from wastewater treatment plants (WWTPs) discharges [1]. In this work, the occurrence and behavior of pharmaceuticals have been investigated from a conventional WWTP in the province of Castelló (Spain). A number of 37 pharmaceuticals from different families as analgesics, benzodiazepines, antibiotics, antihypertensives, etc. have been monitored, among them those included in the European Watch List [2].

Influent (IWW) and effluent wastewater (EWW) 24-h composite samples have been collected over two consecutive days along different campaigns (from April to August 2021). A total of 36 samples have been analysed using direct injection into the liquid chromatography coupled to tandem mass spectrometry based on the methodology developed in our laboratory [3, 4]. Positives for most compounds have been found in the samples collected, and in general the concentrations in IWW have been higher than in EWW samples. The comparison of the daily loads in IWW and EWW waters have allowed the evaluation of removal efficiency of pharmaceuticals from the WWTP investigated. Different behaviors of the compounds have been observed, from total to partial elimination, even poorly eliminated or unremoved. The fact that some pharmaceuticals still remain in EWW samples may suppose a risk for the aquatic environment, which could be solved with additional treatments as well as conducting periodically ambitious monitoring campaigns to prevent the possible negative impact of treated water on the aquatic environment.

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## WC-E10

# STUDY OF THE PHOTODEGRADATION OF PCBs IN WATER BY UV-LED TECHNOLOGY

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Polychlorinated biphenyls (PCBs) are a family of 209 compounds classified as persistent organic pollutants (POPs). PCBs had been synthesized for decades for its use in technical mixtures as heat exchangers and dielectric fluids, due to their chemical stability, high heat transfer capacities, high dielectric constants and low vapor pressures. Even though the production of technical mixtures ceased in late 1980s, these compounds are still present in the environment, and moreover, there are some PCBs that can be unintentionally produced (UP-PCBs) as by-products in a wide variety of chemical processes, such as pigment manufacturing. Given that the generation of these UP-PCBs is different from the synthesis used in technical mixtures, their compositions do not resemble, and consequently, they are not typically monitored.

Despite their hydrophobicity, water is an important pathway of migration for these compounds, either dissolved at low concentrations or particulate-bound. The present work has studied the degradation of PCBs in water samples by UV-LED technology. An analytical methodology based on HRGC-HRMS and quantitation by isotope dilution method has been established for the determination of the pollutants in the samples before and after irradiation. The method allows the identification and quantification of a wide range of PCB congeners, including UP-PCBs, offering recoveries within 67–112 %. For the chromatographic separation an RTX-5 MS column has been employed and for the MS detection an EBE analyzer was used, which allows a resolution of 10000, applying an EI ionization and a VSIR mode for acquisition.

Initially, some irradiation studies were carried out with spiked purified (Elix) water samples in order to evaluate the viability of the process and to obtain information about the photodegradation mechanism. The highest efficacy has been obtained with the simultaneous irradiation at 255, 265 and 285 nm during a 7-hour exposure period using a PearlBeam T 255/265/285 (at a constant distance of 9 cm). Subsequently, the applicability of these processes to real wastewater samples has been studied, both with influent and effluent samples from WWTPs. Irradiation with UV-LEDs achieves a removal of 75–91 % of the total PCB content in effluent samples and a removal of 50–66 % in influent samples.

## WC-E11

# UHPLC-HRMS determination of aerosolized marine biotoxins produced by *Ostreopsis cf. ovata*

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The proliferations of the benthic dinoflagellate *Ostreopsis cf. ovata* have been related to mild respiratory symptoms in people exposed to marine aerosols on some beaches in the Mediterranean Sea. These disorders have been attributed -but not yet fully demonstrated- to palytoxin analogues (PLTX) (ovatoxins -OVTX- and isobaric palytoxin -isoPLTX-) produced by *Ostreopsis*. To evaluate the risk to human health that these events represent, it is necessary to better understand the mechanisms of production of these toxins and their transfer to the atmosphere. Accordingly, in this work we run different laboratory experiments using an aerosol generation tank with microbial communities that were obtained during an *Ostreopsis* bloom in the summers of 2019 [1], 2020 and 2021.

The experiments were run weekly incubating in the laboratory natural microplanktonic communities obtained during *Ostreopsis cf. ovata* blooms (June - August). The experiments were run at a controlled temperature ( $24 \pm 1^\circ\text{C}$ ) using a high-quality stainless steel airtight cylindrical tank (75 L; internal dimensions: 50 cm high, 44 cm diameter) that allowed the generation and collection of aerosols. The concentration of palytoxin analogues in both particulate phase of the seawater and air (aerosols) samples were analyzed. The chromatographic separation of palytoxins analogues was achieved using a Hypersil GOLD C18 column (100 mm x 2.1 mm id., 1.9  $\mu\text{m}$  particle size) packed with totally porous silica particles (Hypersil, Thermo Fisher Scientific) and using gradient elution mode (acetonitrile-water, 0.1% formic acid;  $300 \mu\text{L min}^{-1}$ ). This chromatographic method was coupled to a high-resolution mass spectrometer (Orbitrap) using a heated-electrospray ionization source (UHPLC-HESI-HRMS).

During the experiments in 2019 the cells content was  $10^3$ - $10^4$  *Ostreopsis* cells $\cdot\text{L}_{\text{water}}^{-1}$  and the toxins concentration in the particulate phase was in the range of  $1.1 \times 10^5$  -  $3.1 \times 10^6$   $\text{pg}_{\text{tox}} \cdot \text{L}_{\text{water}}^{-1}$ , while the toxin concentration in the aerosol was estimated at 12–54  $\text{pg}_{\text{tox}} \cdot \text{L}_{\text{air}}^{-1}$ . Then, when it was bubbled after enriching the seawater with a higher abundance of *Ostreopsis* cells ( $10^5$  cells $\cdot\text{L}_{\text{water}}^{-1}$ ) and a higher concentration of toxins in the particulate phase of the water ( $9.3 \times 10^5$  -  $7.9 \times 10^6$   $\text{pg}_{\text{tox}} \cdot \text{L}_{\text{water}}^{-1}$ ) the toxin concentration in the aerosol remained in the same range (11–54  $\text{pg}_{\text{tox}} \cdot \text{L}_{\text{air}}^{-1}$ ). Therefore, no direct relationship was observed between the concentration of *Ostreopsis* cells in the water and the toxin in the aerosol.

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**WC-E12**  
**PYROLYSIS-COMPOUND SPECIFIC ISOTOPE ANALYSIS FOR THE DIRECT  
CHARACTERIZATION OF LIGNIN IN SOILS. IMPLICATIONS FOR TRACING CLIMATE  
CHANGE EFFECTS**

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Lignin in soils is a result of organic matter input and depletion, which is regulated by various factors, such as environmental factors like climate change (temperature, moisture, etc.) [1]. Therefore, lignin is considered an indicator of soil organic carbon storage and dynamics. Given its chemical structure, hence recalcitrance, lignin could be used as a biomarker of processes such as stabilization, mineralization, or biodegradation of soil organic matter (SOM) [2]. The study of C and H isotopes may certainly result in a comprehensive approach to estimate the fate of organic compounds, and to better understand the link between H and C cycles in the soil. The use of C stable isotopes is widely used to investigate sources, evolution, and dynamics of SOM, whilst H stable isotopes provide geographical information and insight into the water dynamics in soils [3].

This communication describes a methodology based on analytical pyrolysis for the direct measure of lignin-derived phenolic compounds specific  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  isotope composition (Py-CSIA). Based on this methodology, we aim to evaluate the  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  isotope composition of lignin-derived phenols as biomarkers of changes in SOM dynamics driven by climatic factors.

Composite dehesa surface (0-10 cm) soil samples (Pozoblanco, Córdoba, Spain) were taken from four forced climatic treatment plots representing warming (W), drought (D), its combination (W+D), and control (D), in two distinct habitats: under evergreen oak canopy and in open pasture. The samples were analysed in triplicate for chemical structural characterization by analytical pyrolysis (Py-GC/MS) and in parallel for  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  (Py-CSIA) using the same chromatographic conditions.

The  $\delta^{13}\text{C}$  average CSIA values ranged from -27.15 ‰ to -33.45 ‰. Significant differences are reportedly driven by the differences in habitat: more depleted values were found in lignin produced in the open pasture than in tree habitat. In addition to the differences reported for habitats, it is observed an  $^{13}\text{C}$  enrichment (up to 7 ‰) associated to the warming (W) treatments. Also remarkable is a gradually  $^{13}\text{C}$  enrichment trend observed in open pasture for siringyl lignin units, that may be attributable to climatic stress.

The  $\delta^2\text{H}$  average values of lignin methoxyphenols varied from -43.92 ‰ to -137.56 ‰. Again, a significant depletion is observed in the open pasture samples. Climatic changes are more pronounced in open pasture, especially in the lignin guaiacyl units. Lignin methoxyl groups from W+D treatment were found significantly enriched in  $^2\text{H}$  relative to other climatic treatments.

This study demonstrates that methoxyphenols  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  values provides a useful tool for inferring climatic processes in soil organic matter in Mediterranean ecosystems. Further discussion on the climatic, environmental processes affecting the isotopic composition of lignin compounds, particularly regarding non-exchangeable hydrogen will be assessed.

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**CLINICAL & PHARMACEUTICAL  
ANALYSIS  
OMICS TECHNIQUES**

## O-CF1

# TACKLING PROTEIN BIOMARKERS THROUGH TARGETED BOTTOM-UP ANALYSIS BY ON-LINE APTAMER AFFINITY SOLID-PHASE EXTRACTION-IMMOBILIZED ENZYME MICROREACTOR CAPILLARY ELECTROPHORESIS-MASS SPECTROMETRY

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In recent years, targeted bottom-up analysis of protein biomarkers is generating a great interest, because it may allow a straightforward, accurate and sensitive measurement of the protein of interest from characteristic signatures of surrogate peptide fragments [1-2]. However, this approach typically requires extensive off-line sample handling for sample clean-up, protein preconcentration and enzymatic digestion before the analysis by high performance separation techniques coupled to mass spectrometry (i.e. LC-MS or CE-MS and -MS/MS). As an alternative, we present a fully integrated valve-free method for the sensitive targeted bottom-up analysis of proteins through on-line aptamer affinity solid-phase extraction-immobilized enzyme microreactor capillary electrophoresis-mass spectrometry (AA-SPE-IMER-CE-MS) [3-4]. The method was developed analyzing  $\alpha$ -synuclein ( $\alpha$ -syn), which is a protein biomarker related to different neurodegenerative disorders, including Parkinson's disease. Under optimized conditions, on-line purification and preconcentration of  $\alpha$ -syn, enzymatic digestion, electrophoretic separation and identification of the tryptic peptides by mass spectrometry was achieved in less than 35 min. The limit of detection was  $0.02 \mu\text{g mL}^{-1}$  of digested protein (66.7% of coverage, i.e. 8 out of 12 expected tryptic peptides were detected). This value was 125 and 10 times lower than for independent on-line digestion by IMER-CE-MS ( $2.5 \mu\text{g mL}^{-1}$ ) and on-line preconcentration by AA-SPE-CE-MS ( $0.2 \mu\text{g mL}^{-1}$ ). The repeatability of AA-SPE-IMER-CE-MS was adequate (at  $0.5 \mu\text{g mL}^{-1}$ , %RSD ranged from 3.7 to 16.9% for peak areas and 3.5 to 7.7% for migration times of the tryptic peptides) and the modified capillary could be reused up to 10 analyses with optimum performance, similarly to IMER-CE-MS. The method was subsequently applied to the analysis of endogenous  $\alpha$ -syn from red blood cell lysates. Ten  $\alpha$ -syn tryptic peptides were detected (83.3% of coverage), enabling the characterization and localization of post-translational modifications of blood  $\alpha$ -syn (i.e. N-terminal acetylation).

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## O-CF2

# SOLUTE INTERACTIONS IN MICROEMULSION LIQUID CHROMATOGRAPHY WITH IONIC LIQUIDS

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Aqueous microemulsions (MEs), where an oil co-exist with water in the presence of the anionic surfactant sodium dodecyl sulphate (SDS), have been proposed as a solution to decrease the amount of organic solvent in the mobile phase needed in reversed-phase liquid chromatography (RPLC) [1]. However, the oil phase of typical MEs is volatile, toxic and flammable, and although it is added in a small amount, it would be convenient to avoid it from an environmental perspective. Recently, the non-polar ionic liquid 1-hexyl-3-methylimidazolium pentafluorophosphate ( $[C_6C_1IM][PF_6]$ ), has been proposed to replace the oil and prepare ionic liquid-in-water MEs for the analysis of phenolic compounds [2]. Based on this report, a procedure was developed to analyze basic compounds ( $\beta$ -adrenoceptor antagonists) at acidic pH (where they exist as cations).

In order to check the possible formation of MEs and elucidate the interactions between the cationic basic compounds and the cations and anions in the additives (the SDS anion, and the ionic liquid cation and anion), an extensive study was made with several methylimidazolium ionic liquids with diverse polarity, where the cations  $[C_2C_1IM]^+$ ,  $[C_4C_1IM]^+$ , or  $[C_6C_1IM]^+$  were associated to the anions  $Cl^-$ ,  $BF_4^-$ , or  $PF_6^-$ , using 1-butanol as co-surfactant. The research focused on the effect on retention and peak profiles produced by the selected ionic liquids to give some insight on the retention mechanisms [3]. The study was performed in comparison with the behavior observed in classical microemulsion liquid chromatography with octane, micellar liquid chromatography with SDS and 1-propanol, and RPLC with mobile phases containing solely the ionic liquids and acetonitrile. A mixture of SDS and a soluble ionic liquid ( $[C_6C_1IM][Cl]$ ), without the addition of alcohol, was also considered as a greener mobile phase in RPLC.

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## O-01

### IN VITRO STUDY OF THE NEUROPROTECTIVE POTENTIAL OF A SUPERCRITICAL EXTRACT OBTAINED FROM DUNALIELLA SALINA MICROALGAE

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Alzheimer's disease (AD) is the most common form of dementia caused by a progressive loss of neurons from different regions of the brain. This multifactorial pathophysiology has been widely characterized by neuroinflammation, extensive oxidative damage, synaptic loss and neuronal cell death. Many studies have suggested that diet and/or food components can prevent the onset of AD due to a complex multi-target therapeutic activity. In the present work, different *in vitro* assays including antioxidant, anti-inflammatory and anti-cholinergic activities of a carotenoid-enriched extract from *Dunaliella salina* microalgae obtained by supercritical fluid extraction are studied. Moreover, its potential neuroprotective effect in the human neuron-like SH-SY5Y cell model against remarkable hallmarks of AD was also evaluated. In parallel a comprehensive metabolomics study based on the use of advanced analytical methodologies was applied to evaluate the effects of the extract in the metabolism of the treated cells. The use of advanced bioinformatics and statistical tools allowed the identification of more than 314 metabolites in SH-SY5Y cells, of which a great number of phosphatidylcholines, triacylglycerols and fatty acids were significantly increased, while several phosphatidylglycerols were decreased, compared to controls. These lipidomic changes in cells along with the possible role exerted by carotenoids and other minor compounds on the cell membrane might explain the observed neuroprotective effect of the *D. salina* extract.

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## OY-01

# The Role of Oxidized Lipids in Fungal Mediated Diseases Using Ion Mobility-Mass Spectrometry.

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Oxylipins are biologically active lipid mediators that play important roles in physio-pathological processes, like infections, cancer, and obesity. Recent findings from our research group have shown that several oxylipins are extremely altered in patients suffering from mucormycosis. These oxidized fatty acids have multiple isomers because of the double bonds and oxidation positions, which can be species-specific [1]. Therefore, its identification could reveal reliable diagnostic markers for the diseases they are involved in. Ion mobility (IM), which allows the separation of molecules based on their spatial configuration, stands out as an excellent tool to study different isomeric oxylipins [2]. In this research, ion mobility-mass spectrometry (IM-MS) was used to identify oxylipins related to mucormycosis.

Oxylipin standards were used to identify those in plasma samples from patients with mucormycosis using an Agilent's 6560 ion mobility Q-TOF LC/MS. The identification was assisted by two features provided by the IM:

- The All-Ions working mode, which provides clean MS/MS spectra by filtering by the drift time (DT) of the precursor ion.
- The High Resolution demultiplexing (HRdm) tool, which improves the resolution in IM throughout a post-acquisition processing that allows the differentiation of unresolved for compounds with very similar collision cross section (CCS).

Elevated oxylipins in infected plasma samples were finally identified based on the comparison of their retention time (RT), drift time (DT), collision cross section (CCS) and fragmentation patterns. These values were used for the creation of an internal database.

Given the wide variety of isomers that comprise oxylipins, IM-MS has shown a great potential for as a further step in their identification. Combining retention time, exact mass, CCS values, highly resolved IM (HRdm) and clean MS/MS fragmentation spectrum (All-Ions) provides unprecedented levels of identification of oxylipin isomers. Moreover, the database is intended to be regularly updated with new oxylipin standards. Finally, applying this technique to samples such as mucormycosis patients allows for a higher identification level and provides new diagnostic approaches for a disease with limited diagnostic confidence.

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## OY-O2

# Differential Modulation of the Central and Peripheral Monoaminergic Neurochemicals by Deprenyl in Zebrafish Larvae

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Zebrafish embryos and larvae are vertebrate models increasingly used in translational neuroscience research [1]. Behavioral impairment induced by the exposure to neuroactive or neurotoxic compounds is commonly linked to changes in modulatory neurotransmitters in the brain. Although different analytical methods for determining monoaminergic neurochemicals in zebrafish larvae have been developed, these models have been used only on whole larvae, as the dissection of the brain of hundreds of larvae is not feasible [2–4]. This raises a key question: Are the changes in the monoaminergic profile of the whole larvae predictive of the changes in the brain? In this study, the levels of ten monoaminergic neurotransmitters were determined in the head, trunk, and the whole body of zebrafish larvae in a control group and in those treated for 24 h with 5 M Deprenyl, a prototypic monoamine-oxidase B inhibitor, eight days post-fertilization. In control larvae, most of the monoaminergic neurochemicals were found at higher levels in the head than in the trunk. Significant changes were found in the distribution of some neurochemicals after Deprenyl- treatment with serotonin and norepinephrine increasing in both the head and trunk, whereas dopamine, L-DOPA, and homovanilic acid levels were only modulated in the head. In fact, the highly significant increase in dopamine levels observed in the head after deprenyl-treatment was not detected in the whole-body analysis. These results indicate that the analysis of neurotransmitters in the zebrafish larvae whole-body should not be used as a general surrogate of the brain.

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## OY-CF1

# Simultaneous determination of 40 drugs of abuse and some metabolites in human urine by SPE followed by LC-MS/MS

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According to the European Monitoring Center for Drugs and Drug Addiction (EMCDDA), Spain has one of the highest amounts of drug use in Europe and is particularly notable for the consumption of cocaine and cannabis. Moreover, during last years, apart from the classic drugs of abuse (DOAs), different synthetic drugs have emerged as important substances in the illegal market, being the new psychoactive substances (NPS) the most important abused synthetic drugs. In this group, the most reported substances are synthetic cannabinoids, synthetic cathinones and synthetic opioids [1].

Different methods have been continuously developed for the determination of different DOAs. However, most of them are focused on particular families [2]. Therefore, in an attempt to provide a multiresidue method able to detect drug polyconsumption, the main aim of the present study was to develop a sensitive methodology for the simultaneous determination of 40 DOAs including classic, synthetic drugs and some metabolites in urine by solid phase extraction (SPE) followed by liquid chromatography tandem mass-spectrometry (LC-MS/MS).

The broad spectrum of chemical properties of the different DOAs included, highlight the importance of studying the sample pre-treatment deeply, and in this sense, different SPE sorbents were evaluated to achieve the highest recovery efficiency. In particular, four different commercial mixed-mode cationic-exchange SPE cartridges were compared: Oasis WCX, Oasis MCX, ExtraBond ECX and ExtraBond SCX.

The present method is capable of determining 40 DOAs at low levels of  $\text{ng mL}^{-1}$ , which enables the detection of these compounds in urine from drug abusers. Finally, 20 urine specimens from women starting a drug-abuse detoxification program were analysed, being cocaine the most detected substance followed by some benzodiazepines. However, no NPS were detected, which demonstrated that even these substances are widely consumed in Europe, they are still not popular in Spain.

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## OY-CF2

# Simultaneous enantiomeric separation of licarbazepine and licarbazepine acetate by electrokinetic chromatography. Determination in pharmaceutical formulations and urine samples.

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Chiral analysis is of crucial importance in many disciplines including the pharmaceutical and bioanalytical fields. This is due to the fact that the biological activity of chiral compounds may reside predominantly in one enantiomeric form. In addition, the targets of drug action are capable to discriminate between enantiomers. Licarbazepine acetate (LicOAc) is a novel anticonvulsant drug indicated for the treatment of epilepsy. LicOAc enantiomers present different pharmacokinetic and pharmacodynamic properties being the S-LicOAc the enantiomer that has a better profile as an antiepileptic drug. This fact makes that it is commercialized as a pure enantiomer (S-licOAc). After its oral administration, it quickly hydrolyzes mainly to the active principle licarbazepine (S-licOH) [1, 2]. Bearing this in mind, chiral methodologies are necessary to ensure the quality control of pharmaceutical formulations commercialized as pure enantiomers and to monitor their hydrolysis products in urine samples.

This work is aimed to develop a fast methodology by Electrokinetic Chromatography for the enantioseparation of LicOAc and LicOH enantiomers so that it could be applied not only to the quality control of S-licOAc in pharmaceutical formulations but also to determine the amount of RS-licOH present in urine samples. Once selected the most appropriate chiral selector to carry out the separation, different experimental conditions were optimized using a Box-Behnken design with three variables (CM- $\beta$ -CD concentration, temperature, and applied voltage) at three levels. The response variables selected were the enantiomeric resolution and the analysis time of RS-LicOH. In addition, a sample treatment based on solid-phase extraction was optimized for urine samples analysis. Finally, analytical characteristics of the developed methodology were evaluated showing good performance for the determination of RS-licOAc and RS-licOH in pharmaceutical formulations and urine samples, respectively, without matrix interferences and achieving limits of detection of 1.2 mg/L for R-licOH and 1.3 mg/L for S-licOH, R-licOAc and S-licOAc.

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## WC-CF1

# MAGNETIC HEADSPACE ADSORPTIVE EXTRACTION PRIOR TO THERMAL DESORPTION-GAS CHROMATOGRAPHY-MASS SPECTROMETRY FOR COLORECTAL CANCER BIOMARKERS DETERMINATION

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Colorectal cancer (CRC) is a leading cause of mortality and morbidity worldwide, expected to cause 2.2 million new cases and 1.1 million deaths by 2030. Early identification of advanced pre-malignant adenomas and removal of these adenomas has been found to decrease CRC incidence and mortality. Colonoscopy is the gold standard for the diagnosis of CRC and fecal immunochemical blood testing (FIT) is the most widely used noninvasive screening tool. Although this screening program has led to a decrease in mortality, its performance is suboptimal, with a fairly good specificity but a high variation in sensitivity leading to missed diagnosis of CRC and performance of unneeded colonoscopies that consume an important amount of resources. Due to these limitations, there is an important need to discover a non-invasive and precise tool for early diagnosis of CRC.

Analytical chemistry researchers are always looking for simple sample preparation techniques to increase selectivity and sensitivity of their determinations with lower total analysis cost. One of these efforts, led to employ magnetic graphene oxide (MGO) nanomaterial as sorbent, supported on a neodymium magnet (Nd), in the extraction technique called Magnetic Headspace Adsorptive Extraction (Mag-HSAE), with improved simplicity, sensitivity and cost effectiveness. This technique has been employed to determine some biomarkers of colorectal cancer disease (i.e., volatile organic compounds) found in fecal samples. The main aim of this study was to develop a new non-invasive method for the diagnosis and prevention of colorectal cancer.

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## WC-CF2

# CAPILLARY ZONE ELECTROPHORESIS OF IMMUNOGLOBULINS OF HEALTH AND FOOD CONCERN

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Immunoglobulins (Igs) are a family, of 150 kDa glycoproteins when in monomeric form, which play important roles in several fields, such as disease biomarkers, pharmaceutical drugs, and functional components in food. At present, most of the top ten best-selling therapeutic drugs are monoclonal antibodies (mAbs), mainly of the IgG class. On the other hand, IgA plays a pivotal role in human colostrum and milk by favoring the early development of the immune system of newborn infants.

Conditions used for production, purification, storage, etc. can modify the chemical structure of glycoproteins, and namely of mAbs. These modifications may affect biological activity, half-life, and immunogenicity of these bio-pharmaceuticals. Similarly, during milk thermal treatment and storage in Human Milk Banks, IgA can be modified and its bioactive properties altered.

These changes in the IgG and IgA molecules can cause variations in their properties, such as size and/or charge giving rise to size variants (e.g. aggregates and fragments) and charge variants (e.g. deamidated forms). Capillary zone electrophoresis (CZE) allows separating analytes based on size to charge ratio, being then an adequate tool to study alterations in the glycoprotein.

This work shows the effect of several parameters, such as presence of excipients, background electrolyte composition and reusability, and capillary separation length on CZE analysis of Igs.

Better resolution is achieved for mAbs variants than for IgA ones. Optimal conditions allow separating the main peak, the acidic variants, and the basic variants for Bevacizumab and Denosumab as well as the mixture of both therapeutic drugs and their charge variants.

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## WC-CF3

# Rapid and sensitive detection of C Reactive Protein in saliva by a sandwich type one-step ELISA method with a smartphone-based reading system

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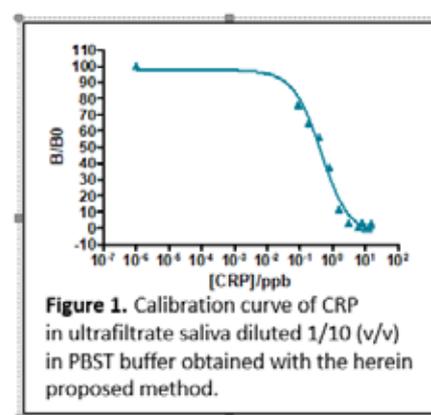
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Human C Reactive Protein (CRP) is an annular (ring-shaped) pentameric protein secreted in the liver as a response to an increase in pro-inflammatory cytokines (mainly interleukin 6), enhanced by interleukin 1 and tumor necrosis factor alpha. Native CRP, soluble in serum and saliva, is considered as an early clinical indicator of sepsis, cardiovascular diseases, cancer, autoimmune disorders such as lupus or rheumatoid arthritis, schizophrenia, etc. [1]. Moreover, CRP has been recently identified as a key biomarker associated with the development of coronavirus disease 2019 (COVID-19) [2].

More widely used diagnostic methods of CRP are based on immunochemical laboratory techniques such as Enzyme-Linked Immunosorbent Assay method (ELISA), and immunoturbidimetric and chemiluminescent assays. However, these methods are time-consuming, requires an invasive sampling of blood; are expensive and complex; and have a low diagnostic sensitivity and a high rate of false negatives. For this reason, there is an urgent need for new analytical tools for rapid and sensitive CRP detection and quantification.

In this work a sandwich type, one-step ELISA method, using a smartphone as a reading system, is proposed for the rapid diagnosis (nearly 50 min) of CRP in saliva. Main analytical characteristics obtained from calibration curves made in ultrafiltrate saliva diluted 1/10 (v/v) in PBST (phosphate-buffered saline with Tween 20) (Figure 1) were: limit of detection < 0,1 ng mL<sup>-1</sup> and a linearity range from 0,1 to 1,0 ng mL<sup>-1</sup>. Furthermore, the ELISA assay was examined in terms of selectivity, repeatability, reproducibility, accuracy and robustness. Finally, it has also been applied to different saliva samples.



**Figure 1.** Calibration curve of CRP in ultrafiltrate saliva diluted 1/10 (v/v) in PBST buffer obtained with the herein proposed method.

This development will be the starting point for the design of a versatile and simple Point-of-Care Testing (PoCT) for CPR in saliva.

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## FAST AND RELIABLE SMARTPHONE-BASED METHODOLOGY TO DETERMINE THE SARS-COV-2 NUCLEOCAPSID PROTEIN IN SALIVA

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Coronavirus disease-2019 (COVID-19) is caused by the RNA virus SARS-CoV-2 [1]. Since other coronaviruses may be responsible of other less dangerous infections, there is an urgent need for developing sensitive and fast accurate diagnostic technologies [2]. In addition, it should be noted that the nucleocapsid protein is the most abundant protein in cells affected by the coronavirus during all states of infection [3].

There are two main types of COVID-19 tests in the market: 1) those used to determine whether the infection is active at this point (PCR or rapid antigen test) and 2) those that detect the presence of antibodies to the SARS-CoV-2 virus. In the last case, the interpretation of results is much more complex, and it cannot be determined if someone has the active infection in such a safe way [4].

This study focuses on determining coronavirus nucleocapsid protein (NPr) in a simple, fast, and reliable way. A new method based on a Smartphone-based colorimetric ELISA assay has been developed to measure this protein in saliva samples in less than 45 min. This method is based on a sandwich type, one-step ELISA. In addition to being a non-invasive methodology, it is portable, low-cost, and easy-to-use. Test results allow us to determine the presence (positive) or absence (negative) of SARS-CoV-2 in saliva



Figure 1. Smartphone-based colorimetric ELISA assay designed for detecting NPr of SARS-CoV-2 in saliva. at the point of the analysis (Figure 1).

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## WC-CF5

# IN-DEPTH COMPARISON OF THE METABOLIC AND PHARMACOKINETIC BEHAVIOUR OF THE STRUCTURALLY RELATED SYNTHETIC CANNABINOIDS AMB-FUBINACA AND AMB-CHMICA IN RATS

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The use of new psychoactive substances (NPS) has dramatically increased in the last years. Among the most consumed families are synthetic cannabinoid receptor agonists (SCRA). As these compounds are, in most cases, completely metabolised, the elucidation of their potential consumption biomarkers in biological samples is required for the detection of drugs intoxications. In this sense, *in vivo* metabolism studies using mice or rats, in combination with high resolution mass spectrometry (HRMS), has proven to be useful for the study and evaluation of the metabolic behaviour of NPS.

In this study, the *in vivo* metabolism and pharmacokinetics of two structurally related SCRA, AMB-FUBINACA and AMB-CHMICA, were evaluated using male Sprague-Dawley rats. Brain, liver, kidney, blood (serum) and urine samples were collected at different times for assessing the differences in metabolism, metabolic reactions, tissue distribution and excretion. Both compounds experimented *O*-demethyl reaction, which occurred more rapidly for AMB-FUBINACA. The parent compounds and the *O*-demethyl metabolites were highly bioaccumulated in liver and they were still found in this tissue 48 h after injection. Due to the different *N*-functionalisation (indazole/indole), different urinary metabolites were formed, some of them being detected even 24h after the injection. Out of the two compounds, AMB-FUBINACA seemed to easily cross the blood-brain barrier, presenting higher brain/serum concentrations ratio than AMB-CHMICA.

### Acknowledgements

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## WC-CF6

# Evaluating the performance of a Collision Cross-Section (CCS) predictor for an enhanced pharmaceutical screening strategy

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The outstanding potential of High-Resolution Mass Spectrometry (HRMS) for target, suspect and non-target screening has been largely reported in the literature. However, the data acquired may sometimes not be sufficient for a reliable identification of the compounds found. The hyphenation of Ion Mobility Separation to HRMS (IMS-HRMS) provides several benefits for suspect analysis to improve the confidence in the identification of pharmaceuticals in complex matrices.

IMS allows an additional separation of compounds based on their shape, chemical structure and three-dimensional conformation. The drift-time measured can be translated to Collision Cross-Section (CCS) values which result in a compound unique parameter that could even help differentiating isomeric and isobaric compounds. As a consequence, the identification of pharmaceuticals can be refined by including this additional parameter into the set identification criteria [1]. Hence, knowing an ion's CCS values enables the detection of analytes and reduces the occurrence of false positives [2]. Yet, due to the recent development of such technique, the number of empirical CCS values is still limited. Consequently, the prediction of CCS is pivotal for enhancing the aforementioned types of analysis [3]. In this work, the performance of a CCS predictor by means of Artificial Neural Networks (ANNs) has been evaluated for a suspect pharmaceutical screening. The potential of ANNs to provide an accurately predicted CCS values for pharmaceuticals has been demonstrated, since all predictions were deviated less than 3.5%, below the 6% error with a 95% confidence interval reported in the literature.

### Acknowledgements

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## WC-CF7

### NATURAL TATTOOS AND DYES: TRULY HARMLESS?

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Temporary tattoos can be included in the group of new format cosmetics [1,2]. In recent times, the use of natural pigments from plants such as famous henna tattoos or even the innovative jagua tattoos, has been increasingly explored. Henna contains lawsone as an active ingredient. Jagua contains geniposide and its bioactive compound, genipin, both of which can be potential new allergens in temporary tattoos [3, 4]. Their non-formulated regulations, the lack of labeling and the fact that they are sold on well-known websites cause insecurity. Until now, there has been little research on emerging natural pigment-based temporary tattoos, their constituents and potential health impact.

On the first part of this work, the development of an analytical method for the quality control analysis of these complex samples and to determine their active ingredients is proposed [5]. The initial results obtained to prove the authenticity of this type of dyes according to their markers (lawsone in henna, genipin and geniposide in jagua) are presented. Thus, possible frauds in products sold as natural henna can be uncovered.

On the second part of the work focuses on the in-depth characterization of the active compounds by ultra-high performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry (UHPLC-QTOF-MS) [6]. At the same time, a novel non-targeted characterization is applied for this type of samples, searching for compounds ranging from the original ingredients to other allergens or additives of interest that they may contain.

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## WC-O1

### LIVER CHANGES ASSOCIATED WITH ANTIOXIDANTS SUPPLEMENTATION IN WISTAR RATS WITH INDUCED STEATOHEPATITIS: THE POTENTIAL OF UNTARGETED METABOLOMICS

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Oxidative stress and inflammation have been widely evidenced to be determinants in the NAFLD (Non-alcoholic fatty liver disease). Having studied previously the effect that resveratrol and pterostilbene had on the progression or slowing down of this disease to more severe stages, the aim of this complementary study is to determine the metabolic changes that occur in a rat liver with induced NAFLD by dietary administration of these compounds. To this effect, untargeted metabolomics approach with the novel combination of ion mobility separation coupled to high resolution mass spectrometry (IMS-HRMS) have been applied in order to determine impact of resveratrol and pterostilbene intake to the metabolic profile of the wistar rats liver with induced NAFLD. RP-LC and HILIC in both ionization modes were employed to analyze the liver metabolome fingerprint of male Wistar rats (n=50) fed with five experimental diets either standard (CC) or a high-fat and high-fructose diet (HF), supplemented or not with resveratrol (RSV30, 30 mg/kg/d) or pterostilbene (PT15 or PT30, 15 or 30 mg/kg/d, respectively). After univariate and multivariate statistical analysis, a total of 36 endogenous compounds present in the liver were elucidated as markers of the different diets administered. The IMS has demonstrated to be an improvement in the elucidation process and it allowed the obtention collision cross section value (CCS) as additional structural descriptor which could be compared with available libraries and provide more confidence in the identification [1].

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## WC-O2

# Quantitative large scale metabolomics platform for characterizing the human exposome

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Metabolomics is nowadays one of the most powerful technologies for holistically deciphering the molecular mechanisms driving the final phenotype, which is influenced by multiple biological and lifestyle conditions (e.g., disease, genetic background, xenobiotics). Emerging evidence highlights the prominent involvement of environmental factors in health status, including the diet, drug consumption and exposure to pollutants, i.e. the exposome. However, novel tools are needed for comprehensive metabolomics analysis, preferably in a quantitative manner to allow for cross-cohort comparisons.

We have developed a large scale quantitative platform for comprehensive and rapid metabolomics fingerprinting of common biological samples [1]. The methodology is based on the application of simple and robust in-plate extraction protocols (SPE and dilution for urine, protein precipitation for serum/plasma) and subsequent analysis by reversed-phase ultra-high performance liquid chromatography coupled to tandem mass spectrometry [2-3]. This enables the simultaneous quantitation of more than 1000 metabolites in very short run times and using low volumes of biological sample. The coverage of this method comprises about 450 food-derived metabolites, 40 common pollutants (e.g., pesticides, phthalates, parabens), 40 pharmaceuticals, and some other biomarkers related to lifestyle habits (e.g., smoking, alcohol consumption), thus providing a comprehensive and accurate characterization of the human exposome. This metabolomics approach also includes around 500 endogenous metabolites involved in central biochemical pathways, covering a broad range of chemical classes: amino acids and derivatives, organic acids, biogenic amines, carbohydrates, vitamins, lipids. To construct this metabolite library, we also considered the central role of microbiota on detoxification processes, metabolism and health.

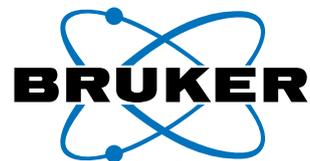
To sum up, this novel platform represents one-step further towards comprehensive metabolomics-based exposome research. The rapidity and low sample requirements of this methodology facilitate its implementation in large epidemiological studies.

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**O-F1**  
**DEVELOPMENT AND VALIDATION OF A METHOD**  
**FOR THE COMPREHENSIVE INSPECTION OF EXPERIMENTAL DESIGNS IN HPLC**

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In liquid chromatography, the basis of interpretive optimisations is the prediction of resolution provided by appropriate retention models. The quality of such predictions depends critically on the information given by the training experimental designs. In this work, a general methodology based on the error propagation theory was developed and validated for assessing the quality of training designs. Accordingly, the uncertainties associated to the prediction of retention times are systematically evaluated by measuring the susceptibility of the model parameters to changes in the elution conditions, in either isocratic or gradient conditions. Relative uncertainty plots in predictions are given, which provide significant and interpretable results. The magnitude of the uncertainties, together with the systematic, coherent and logical changes observed at decreasing solute polarity, give support to the results. The Neue-Kuss equation was selected to model the retention of a set of 14 sulphonamides with different polarity.

The work was also aimed to give some recommendations useful to construct experimental designs with good prediction performance. Isocratic training designs, which in the literature are widely accepted as the most informative, were confirmed as the best. As a general conclusion, gradients were predicted with intrinsically smaller uncertainties, independently of the training experimental design. In addition, gradient predictions were more insensitive than those isocratic with regard to the type of training design. The final purpose is the evaluation of multiple designs, including families of related designs (single or multi-isocratic, linear or multi-linear gradients, mixed isocratic-gradient designs, or any other) when they are varied systematically (e.g., with different slopes, distributions or number of experiments).

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## O-ND1

# Controlled atmosphere flexible microtube plasma soft ionization source: a promising tool for the determination of small molecules by GC-MS in the field of clinical and food analysis

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Although electron impact ionization (EI) remains the standard ionization source for GC-MS, it presents extensive fragmentation as its main limitation. The potential of a novel plasma-based soft ionization source, controlled-atmosphere flexible microtube plasma (CA-F $\mu$ TP), has been evaluated for food safety and clinical applications. Therefore, the sensitive ionization of volatile organic biomarkers relevant for cancer was carried out. Besides, the determination of monoaromatic volatile BTEX group (namely benzene, toluene, ethylbenzene, and o-, m- and p-xylenes) in olive oil, based on headspace technique, was also evaluated. The obtained results show an attractive advantage over EI due to no fragmentation was observed. [M+NO]<sup>+</sup> was obtained as the most abundant ion for BTEX. In contrast, the protonated molecule [M+H]<sup>+</sup> was obtained by proton transfer reaction for all biomarkers studied as ketones. This fact is due the most abundant reactants ions generated in this ionization source are NO<sup>+</sup> and (H<sub>2</sub>O)<sub>2</sub>H<sup>+</sup>. Sample treatment for human saliva is described, and relevant candidate biomarkers are measured in the saliva matrix, showing a very good ionization efficiency and neglectable matrix effects with LOD below 800  $\mu\text{g L}^{-1}$ . In the case of BTEX, sensitivity for CA-F $\mu$ TP was comparable to those obtained by EI, achieving LODs ranged from 0.6 to 1.0  $\mu\text{g kg}^{-1}$ . In this work, the applicability of the CA-F $\mu$ TP ionization source has been demonstrated. The CA-F $\mu$ TP offered a soft ionization and an adequate sensitivity for several compounds. The proposed interface provided a no fragmented spectrum, being [M+NO]<sup>+</sup> or [M-H]<sup>+</sup> the most abundant ions formed. By contrast, a significant fragmentation was observed using EI source. This feature makes the CA-F $\mu$ TP ionization source a promising tool for non-target analysis, in which the spectral libraries could not identify unknown compounds.

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## O-ND2

# INSIGHTS OF TUBE PLASMA AS A NEW ION SOURCE FOR GC-MS COUPLING

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In the last decade, atmospheric pressure ionization (API) sources are creating a great expectation for GC-MS coupling. These soft sources present several advantages over traditional high-vacuum ionization techniques such as the preservation of the molecular or *quasimolecular* ion which overcomes the compromise between sensitivity and selectivity and the possibility to promote specific ionization mechanism using chemical reagents. Additionally, API sources allows to switch from LC- to GC-coupling using the same mass spectrometer, which significantly reduces the instrumental cost in the laboratories [1].

The development of API sources for GC-MS might open new scenarios for the detection of a wider range of compounds as atmospheric pressure photoionization (APPI) and especially atmospheric pressure chemical ionization (APCI) have shown in different application fields such as food analysis, environmental analysis or drug and clinical analysis, among others [2,3]. However, there is still a long way of improvement and, thereby, new API sources and set-ups have been recently investigated to provide new ionization mechanisms as well as to overcome some difficulties such as response stability or memory effects.

Here we present a tube plasma (TP) source for GC-MS. This TP design consists of a quartz tube as the dielectric and a stainless-steel needle-shaped electrode. The electrode is positioned inside the dielectric tube and connected to a high voltage pulser. This TP probe is positioned inside an open atmosphere ionization source chamber on a way the GC eluate passes the plasma region on axis with the mass spectrometer inlet. Different plasma gases (He, Ar, synthetic air, etc.), geometrical and TP-related parameters as well as source conditions were evaluated to provide an efficient and selective ionization for a wide range of compounds with non- or a minimal in-source fragmentation. Moreover, some quality parameters were determined to show the good performance of the source in terms of precision, memory effects and detection capability. The ionization was also compared to other API sources in order to show the range of compounds TP would be able to detect. Finally, as a case of study, the TP source was applied to the analysis of the volatile fraction of several herbal liqueurs by GC-HRMS (QTOF). The results were compared with those obtained by GC-MS using electron ionization (EI) showing the great potential of this source also for non-targeted analysis.

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## OY-S1

# Combining microfluidic paper based platform and metal-organic frameworks in a single device for phenolic content assessment in fruits

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Over the last decades, several epidemiological studies have shown that the consumption of vegetables and fruits is beneficial for the human health and there is an association between plant-based diets and lower cardiovascular diseases. These benefits, together with other characteristics like colour and flavor, may be attributed, in part, due to the presence of phenolic compounds (PC) [1]. Since different fruits differ markedly in the quantity and types of phenolic antioxidants and their conjugates, there is a necessity to monitor these compounds with simple and fast methods.

In this context, the use of greener approaches like microfluidic paper-based analytical device ( $\mu$ PAD) can be an effective alternative to those time-consuming methods using traditional spectrometric equipment. The advantages are not only based on the reduction of required volume and waste production, but also in the hand size and portability. In this work, a  $\mu$ PAD has been designed for the PC quantification based on the well-known Folin-Ciocalteu reaction [2]. A minimum pretreatment of sample (squishing and filtering) was highly encouraged in order to do the analysis on-field. For this purpose, the combination of metal-organic frameworks (MOFs) with  $\mu$ PAD with pretreatment purposes is presented for the first time, as far as we know. Taking advantage to the MOF properties, namely large surface areas (ca. 1400 m<sup>2</sup> g<sup>-1</sup>) and high porosities [3], its use in the  $\mu$ PAD assembly allows the isolation and pre-concentration of analytes from complex samples. This approach enables to solve typical problems such as low sample volumes and high LOD. In so doing, several parameters referring to the  $\mu$ PAD construction were optimized including type and amount of MOF (previously characterized), sample volume and the effect of interferences. The analytical features were also studied obtaining a linear range comprised between 0 and 30 mg L<sup>-1</sup>, LOD up to 0.5 mg L<sup>-1</sup> and acceptable precision (RSD < 14 %). Finally, the method was successfully applied to the quantification of PC in several fruit samples.

### Acknowledgements

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## OY-S2

### Determination of veterinary drugs and pesticides in salmon using liquid chromatography/tandem mass spectrometry using a specific sample cleanup

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Fish products are amongst the most consumed foodstuffs due to the changes in eating habits in the last decades. Aquaculture has been responsible for the continuing growth in the supply of fish for human consumption, whereas capture fishery production has been relatively static since the late 1980s. The crash cultivation methods applied in aquaculture imply a higher concentration of animals, reduced spaces, and the use of formulated feeds containing veterinary drugs and pesticides, among other substances. European Union Commission Regulation 37/2010 fixes the maximum residue limits (MRLs) of veterinary drugs in animal-origin foodstuffs. Although several studies reveal that pesticide residues are present at substantial concentration levels in fish, yet MRLs are to be established in fish products by the European Union. With this in mind, the development of multi-residue methods with high sensitivity and selectivity for determining these organic contaminants in fish samples at  $\mu\text{g kg}^{-1}$  levels is relevant.

This work evaluated a novel sample treatment approach based on a modified QuEChERS method for the simultaneous determination of veterinary drug and pesticide residues in salmon. To improve the QuEChERS performance, Enhanced Matrix Removal-Lipid dSPE cleanup sorbent was evaluated for the first time for the simultaneous analysis of these organic contaminants in salmon samples. Due to this sorbent can effectively remove coextracted families of lipids. To cover a wide range of polarities, 65 pesticides and 41 veterinary drugs with log Kow ranging from  $-1.4$  to  $5.5$  were selected. Extracts after cleanup were analyzed by ultra-high-performance liquid chromatography-tandem mass spectrometry for analyte confirmation and quantitation. Outstanding results were obtained for both extraction efficiency and matrix removal. A negligible matrix effect was obtained for 57% of the studied compounds, whereas the rest presented a soft matrix effect. The recovery for spiked samples was in agreement with the current European Union recommendations for most compounds. The rest of the parameters were also satisfactory, reaching quantification limits lower than  $3.7 \mu\text{g kg}^{-1}$  in all cases. The precision was better than 20% in all cases. Finally, the method performance was successfully demonstrated with 20 salmon samples, five of which contained pesticide or veterinary drug residues.

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# OY-ND1

## HAND-HELD DIODE LASER FOR ON-SITE ANALYSIS USING TRANSPORTABLE MASS SPECTROMETRY

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Rapid and easy-to-perform methods for on-site analysis have a bright future in forensic, environmental, and food analysis [1]. On-site prescreening of samples for target compounds will reduce the number of suspicious samples transported to the laboratory for analysis and make control and monitoring systems more effective. Ambient ionization mass spectrometry (AIMS) techniques have been developed, offering simplified sample preparation and sample introduction protocols prior to analysis. So far, only a few studies have reported ambient ionization of food contaminants and drug analysis with a (trans)portable MS system [2,3].

In this work, a hand-held laser diode thermal desorption electrospray ionization (LDTD-ESI) mass spectrometry (MS) method was developed for rapid screening of illegal substances in solid samples. A simple, inexpensive, battery-powered surgical laser diode at 940 nm was employed to ablate the solid samples. After ablation, the ionization occurs by means of nano-ESI. Among the optimized ESI parameters, the solvent (methanol/water, 50:50, v/v) and the flow rate (50  $\mu\text{L h}^{-1}$ ) were critical to obtain the best sensitivity. In addition, a black polytetrafluoroethylene substrate was investigated and demonstrated to enhance the desorption of the analyte to the gas phase.

The applicability was demonstrated to rapidly identify selective androgen receptor modulators (SARMs) in pills and powders based on accurate mass measurements by time-of-flight MS. Also, the hand-held LDTD-ESI was combined with a transportable single quadrupole MS. The same SARMs samples were analyzed, and identifications were based on in-source cone voltage fragmentation patterns observed. These initial results demonstrate the applicability of the developed simplified LDTD-ESI MS method for future on-site testing of organic compounds in solid samples [4].

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## OY-ND2

### Exploring GC-APCI-IMS-HRMS possibilities for the screening of organic micropollutants.

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Ion mobility separation coupled to high resolution mass spectrometry (IMS-HRMS) provides extra valuable information in screening approaches of organic micropollutants in complex matrices. IMS allows to separate species of interest from co-eluting matrix interferences and/or resolve isomers based on their charge, shape and size being IMS-derived collision cross section (CCS) a robust parameter comparable between instruments [1].

Excellent separation power of gas chromatography (GC) combined with improved identification properties of HRMS is a powerful tool for identification and structure elucidation of unknown (semi) volatile compounds. Oppositely to electron ionization (EI), the soft ionization promoted by atmospheric pressure chemical ionization (APCI) source designed for GC allows a rapid and wide-scope non-target and suspect screening based on the investigation of the molecular ion and/or protonated molecule [2].

In the current study, the coupling between GC-APCI and IMS-HRMS has been used. A CCS library was built containing 264 relevant multi-class organic pollutants in environmental and food fields, comprising information regarding CCS for molecular ion and/or protonated molecules and some in-source fragments. Based on mobility data provided, the CCS values for both species were compared, and the possibility of separating isomers was explored, as well as the feasibility of employing CCS databases acquired by liquid chromatography-electrospray-IMS-HRMS. Moreover, the potential power of IMS was assessed in complex-matrix samples, such as feed fish extracts. The results reported in this work are of special interest for those researchers working on wide-scope screening of GC-amenable organic compounds.

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# WC-S1

## DEVELOPMENT AND VALIDATION OF A METHOD FOR THE ANALYSIS OF HALOPHENOLS AND HALOANISOLES IN CORK MACERATES BY SBSE-GC-GC-(NCI)MS EMPLOYING NCI AS IONIZATION SOURCE

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Halophenols and haloanisoles are among the most important compounds responsible for “cork taint” in wine. This fault is usually described by musty/mouldy odors that overwhelm the bouquet of wine. Compounds such as 2,4,6-trichloroanisole (TCA) and 2,4,6-tribromoanisole (TBA) have odor thresholds between 1 and 8 ng/L. Additionally, they suppress the olfactory sensitivity [1]. Hence, the presence of these compounds at trace levels in wine can ruin a significant amount of bottles, causing important economic losses.

Commonly, the analysis of halophenols and haloanisoles has been mainly devoted to wine analysis. However, it is known that these compounds come from the cork stoppers and originally from the natural cork employed in their manufacturing. In this work, we propose a method based on the extraction of 13 halophenols and haloanisoles involved in cork taint formation by maceration during 24 hours of ground natural cork with a hydroalcoholic solution (adapted from the method for cork stoppers by the International Organization of Vine and Wine (OIV)) [2]. Subsequently, cork macerates were extracted with a PDMS-coated stir bar. Concentration of salt, pH, time and type of SBSE were optimized and 20% NaCl and pH 3.5 at 500 rpm for 1 hour were chosen. Then, stir bars were submitted to thermal desorption and analysis in a single-oven heart-cut gas chromatograph operated with a Dean’s switch to divert to the 2<sup>nd</sup> column the chromatographic cuts corresponding to the target compounds on the 1<sup>st</sup> column, and finally being analyzed by the mass spectrometer. Negative Chemical Ionization (NCI) with methane as reagent gas gives a superior sensitivity for the analysis of compounds containing halogen atoms, the method was validated achieving limits of detection (LOD) well below the reported sensory thresholds.

In this regard, LOD were 0.80 ng/L for halophenols and 0.049 ng/L for haloanisoles, respectively. Linearity was satisfactory with  $r^2 > 0.98$  in all cases and repeatability of a cork macerate spiked at 0.195 and 6.25 ng/L gave a %RSD (n=3) of 13 and 7%, respectively. Matrix effects were observed by the calibration curves obtained in a blank cork macerate and a hydroalcoholic solution requiring a matrix-matched calibration. Finally, the proposed method was applied to the determination of 48 natural cork samples from different origin.

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## WC-S2

### DEVELOPMENT OF NEW SILICA-BASED MIXED MODE ION-EXCHANGE SORBENTS

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Nowadays, sample preparation is becoming more and more relevant to improve the selectivity and sensitivity of analytical methods. In the case of sorptive techniques, these features are thanks to the selection of suitable materials<sup>[1]</sup>. Mixed mode ion-exchange sorbents retain compounds through hydrophobic and ion-exchange interactions. Selectivity can be achieved since an effective clean step can be included during the extraction protocol<sup>[2]</sup>. Mixed mode ion-exchange sorbents that are commercially available are only based in one type of ion-exchange interaction, either anionic or cationic interactions and this may be a limitation. Two zwitterionic sorbents have been synthesized and evaluated through solid phase extraction (SPE), in the determination of drugs in water samples. These materials are based on a silica network with the same functionalization: C<sub>18</sub> chains, quaternary amines, and sulfonic groups, to perform hydrophobic, anionic, and cationic interactions respectively. The difference between them is the presence of embedded carbon microparticles in the silica skeleton.

Both materials were initially optimised for the determination of basic and acid drugs. However, the sorbents displayed selectivity for the basic compounds, therefore, the analysis of complex samples was carried out only for these compounds.

After the optimization of the SPE protocol, both materials were evaluated with environmental water samples using LC-MS/MS. The results showed that the sorbent without carbon microparticles provided better results. Thus, this sorbent was employed for method validation and for the analysis of water samples from river and effluent wastewater treatment plants.

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## WC-S3

# DETERMINATION OF PHTHALIC ACID ESTERS AND DI(2-ETHYLHEXYL) ADIPATE IN COFFEE OBTAINED FROM CAPSULES

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In recent years, phthalic acid esters (PAEs) have gained great interest for the scientific community as a result of their negative effects on human's health and also due to their wide use as plasticizers that, in combination with current global problems related to plastics pollution, have made PAEs ubiquitous chemicals. Of particular relevance is the presence of these compounds in food packaging due to their migration ability (food ingestion is the main source of human exposure [1]), which have yielded in the regulation of their use by different governments and organizations as well as in the establishment of specific migration limits for some of them, in particular, in plastic materials intended to be in contact with food.

In the present work, a group of 9 PAEs (dipropyl phthalate, DPP; diisobutyl phthalate, DIBP; dibutyl phthalate, DBP; diisopentyl phthalate, DIPP; di-n-pentyl phthalate, DNPP; dihexyl phthalate, DHP; butyl benzyl phthalate, BBP; dicyclohexyl phthalate, DCHP; and di(2-ethylhexyl) phthalate, DEHP) and di(2-ethylhexyl) adipate (DEHA) has been studied in coffee samples of different intensity and caffeine content prepared from commercial plastic and aluminium capsules. In order to analyse the selected compounds, the ammonium formate version of the QuEChERS method has been used [2] followed by gas chromatography-mass spectrometry, being the first time that this QuEChERS version has been applied for the determination of PAEs and DEHA in coffee samples. The proposed method allowed obtaining recovery values in the range 70-120% and RSD values below 20% for most of the analytes in the different coffee varieties, as well as a low amount of matrix co-extractives. The lowest calibration levels of the method were in the range 0.5-5 µg/L. Several samples of each type of coffee were also analysed, finding DBP, DEHA and DEHP in decaffeinated samples, but below the tolerable daily intake established for some of them.

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## WC-S4

# Determination of phthalic acid esters and di(2-ethylhexyl) adipate in fish and squid using the ammonium formate version of the QuEChERS method combined with gas chromatography mass spectrometry

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The demonstrated endocrine disrupting activity or reproductive toxicity of phthalic acid esters (PAEs), together with their known ability to migrate to the surrounding media, have intensified the study and control of these compounds in different environmental compartments, not only by the scientific community, but also by different governmental organizations [1]. In this sense, the discharge of wastewater and plastics has caused many of these compounds to be present in oceans around the world and, therefore, they can affect the marine organisms that inhabit them. In particular, the subsequent ingestion of these organisms may constitute an important source of PAEs exposure by humans.

In the present study, the ammonium formate version of the QuEChERS method [2], was applied for the first time to extract a group of twelve PAEs and one adipate from two species of fish (*Scomber colias* and *Katsuwonus pelamis*) and one of squid (*Loligo gahi*). The lowest calibration levels of the method were in the range 0.5-10 ng/g and the mean recovery values between 70 and 117% with relative standard deviation values  $\leq 20\%$ . Soft matrix effects were found for most analytes and matrices, except in squid samples, for which they were mostly medium with a moderate ion suppression. The analysis of 10 samples of each type showed the presence of DIBP, DBP and DEHP in some of the samples and species, but at concentrations still not representing concerning values for humans.

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## WC-S5

### A new sustainable analytical method to determine plastic migrants in jellies

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Phthalates are the most common plasticizers used to provide greater flexibility, durability, and heat resistance to plastics like polyvinyl chloride [1]. Since these compounds are not covalently linked to the plastic matrix, they can easily transfer to other materials they are in contact with, like food products. This is the main route of exposure of population to this family of compounds, which could potentially produce health issues since phthalates can act as endocrine disruptors [2]. Because of that, developing better and more sustainable methods to determine plastic migrants in food products is vital to assure the healthiness and safety of the agri-food industry.

In this context, a new analytical method to determine a group of six phthalates and one adipate in jellies has been developed using the magnetic micro-dispersive solid phase extraction with Fe<sub>3</sub>O<sub>4</sub> nanoparticles covered with polyaniline (PANI) as sorbent, and the ultra-high-performance liquid chromatography coupled to tandem mass spectrometry as separation and detection techniques. Recovery study demonstrated the excellent performance of the method showing values in the range of 70-123% with relative standard deviations (RSDs) lower than 19. Besides, Limits of Quantification (LOQ) of the method were calculated for each analyte, showing values in the range of 11.1-64.1 ng/L. Finally, the method was applied for the determination of plastic migrants in a group of 10 commercial jellies. The results showed its ability to ensure the safe consumption of these products by indicating the concentration of most analytes below the LOQ, whereas DEHA was quantified in one sample packed in a plastic container at a concentration of 6.85 µg/L.

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## WC-S6

# GREEN ASSESSMENT OF PLASTIC MIGRANTS IN BOTTLED WATERS. STUDY OF THE EFFECT OF TEMPERATURE AND STORAGE TIME

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The increasing consumption of bottled beverages, especially bottled water, is becoming more and more noticeable. Concretely, Spain ranks fifth in Europe with an average consumption of 135.5 liters per capita [1]. However, as it is known, certain plastic containers can be detrimental to the consumers health since harmful substances can migrate into drinks, which is severely affected by long storage time and temperature variations. Among them, phthalates, additives used during the manufacture of plastics, are a well-known group of endocrine disruptors capable of posing a health risk among the population even at very low concentration [2]. Therefore, it is necessary to monitor and control this group of compounds that are found at trace levels in samples with highly selective and sensitive methods.

With the greatest concern for the environment and the search for more sustainable systems, in Analytical Chemistry, deep eutectic solvents (DES) have appeared as the solvents of tomorrow, showing high biocompatibility and biodegradability, emerging as low-cost replacement of other most toxic solvents [3].

In this context, the aim of this work is to carry out an evaluation of the effect of temperature and storage time on the migration of phthalates from bottled waters commercialized in the Canary Islands, applying a natural hydrophobic DES-based liquid-liquid microextraction and the ultra-high performance liquid chromatography-tandem mass spectrometry as extraction, separation and determination techniques, respectively.

### Acknowledgements

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**WC-S7**  
**DEVELOPMENT OF A VORTEX-ASSISTED DISPERSIVE LIQUID-LIQUID  
MICROEXTRACTION FOR THE ANALYSIS OF ALKYLPHENOLS, BISPHENOLS AND  
ALKYLPHENOL ETHOXYLATES IN MICROBIAL-FERMENTED DRINKS**

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Dispersive liquid-liquid microextraction (DLLME) is a well-established alternative to classical LLE extractions. Deep eutectic solvents (DES) have emerged as substitutes of the classical organic solvents initially employed in this technique [1]. These materials remain liquid over a wide range of temperatures and are characterized by having a significantly lower melting point than those of the specific constituents. Regarding DLLME, hydrophobic DES (HDES) are particularly interesting since they can be used with aqueous matrices without additional components. From a Green Chemistry perspective, so-called natural DES (NaDES) are fundamental because the individual components are abundant natural compounds [1].

Microbial-fermented beverages have gained increasing interest due to their alleged health benefits (e.g. delayed ageing, blood detoxification, improvement of gastrointestinal and glandular functions, etc.) [2]. Among them, kombucha and water kefir have become quite popular. However, the potential contaminants in these food matrices have not been analyzed yet. Alkylphenols, bisphenols and their metabolites (including alkylphenol ethoxylates) have been identified as substances of concern due to their estrogenic mimicking effect and other adverse consequences. Due to their important industrial use, their residues may enter the food chain and the development of efficient analytical methodologies is essential.

In this work, a new vortex-assisted DLLME, based on a NaHDES, was developed for the analysis of 13 alkylphenols, bisphenols and alkylphenol ethoxylates in bottled water, kombucha and water kefir. Adequate recovery values (in the range 70-121%) and limits of detection (0.10 ng/L - 2.99 µg/L) were obtained. This is the first time that kombucha and water kefir have been analyzed to determine xenobiotic contaminants.

#### **Acknowledgements**

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# WC-F1

## CHARACTERIZATION OF HILIC COLUMNS: RETENTION MODES AND SOLVENT VOLUMES

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Hydrophilic Interaction Liquid Chromatography (HILIC) is an especially suitable tool for the determination of polar analytes of biological interest. However, the mechanisms responsible for the chromatographic retention are complex and currently under study. The main retention mechanism in HILIC is based on analyte partitioning between the bulk mobile phase and hydroorganic water-rich layers of reduced mobility, partially adsorbed on the polar bonded phase and chromatographic support. Therefore, in contrast to reversed-phase liquid chromatography (RPLC), the volumes of both the mobile and the stationary phases depend on the water content and composition of the eluent [1,2].

In the present work we present a methodology for the estimation of the hold-up volume ( $V_M$ , mobile phase volume inside the column) based on a homologous series derived from the Abraham's solvation parameter model [3]. This is a fundamental parameter in the measurement of accurate retention factors ( $k$ ), which are necessary for retention modeling. Additionally, this approach provides information about the predominant retention mode of a column: the expected HILIC behavior at high contents of organic solvent in the eluent (acetonitrile or methanol) or even RPLC in water-rich mobile phases. At intermediate compositions a dual HILIC-RPLC behavior is observed.

The volume of the water-rich transition layers ( $V_L$ ) acting as stationary phase can be determined from the previously mentioned hold-up volume and the total solvent volume inside the column ( $V_{\text{solvent}} = V_M + V_L$ ). The latter can be obtained from pycnometric measurements using pure water and organic solvents (acetonitrile or methanol) as eluents due to their sufficiently different densities. Finally, from the determined  $V_L$  and column weight it is possible to estimate the mean composition of these water-rich transition layers [4].

Several HILIC columns with diverse functionalization (zwitterionic sulfobetaine, zwitterionic phosphorylcholine, aminopropyl, pentafluorophenyl, polyvinyl alcohol, and 1,2-dihydroxypropyl) were characterized in this work, involving different homologous series ( $n$ -alkyl benzenes,  $n$ -alkyl phenones, and  $n$ -alkyl ketones) for  $V_M$  determination [5].

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# WC-ND1

## ATMOSPHERIC PRESSURE PHOTOIONIZATION – A RELIABLE AND FEASIBLE SOURCE FOR GC-HRMS DETERMINATION OF ENVIRONMENTAL POLLUTANTS

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Over the years, environmental pollution has become a serious threat to humans and wildlife, causing harmful effects on living organisms and rapid deterioration of natural resources. Among them, halogenated organic contaminants are of great concern since most of them are endocrine disruptors and can cause neurotoxicity and immunotoxicity. Furthermore, they are persistent, bioaccumulate through food webs, and can be transported over long distances [1]. Generally, the determination of halogenated pollutants is currently carried out by gas chromatography coupled to mass spectrometry and, depending on the family of compounds, different ionization techniques such as electron ionization (EI) and electron-capture negative ionization (ECNI) are usually used. However, problems related to low ionization efficiency, the formation of nonspecific ions, or the occurrence of internal interferences have been reported for some environmental pollutants. Recently, GC-MS analysis has been moving from classical ionization techniques to atmospheric pressure ionization (API) to broaden the range of analysed compounds and improve their ionization and detectability [2,3]. In this way, the atmospheric pressure chemical ionization (APCI) and atmospheric pressure photoionization (APPI) can be excellent alternatives to the classical EI and ECNI for the determination by GC-MS of halogenated contaminants, although their use is still limited.

The present work aims to demonstrate the capability and potential of the new coupling GC-APPI-HRMS (Orbitrap) for the accurate and precise determination of several families of legacy and emerging environmental contaminants including, neutral per- and polyfluoroalkyl substances (nPFASs), polychlorinated dibenzo-*p*-dioxins, and dibenzofurans (PCDD/Fs), dioxin-like polychlorinated biphenyls (dl-PCBs), polychlorinated naphthalenes (PCNs), short-chain chlorinated paraffins (SCCPs), and Dechlorane Plus (DP) and analogues. To this end, different strategies based on direct and dopant-assisted ionization, or anion-attached ionization, were applied to achieve maximum sensitivity and selectivity in the determination of the target compounds. The performance of the developed GC-APPI-HRMS methods was assessed by establishing their quality parameters and comparing them with those published using traditional methodologies. The applicability of the GC-APPI-HRMS methods was validated by analysing the target compounds in selected environmental samples with a wide range of concentration levels. The results and conclusions of the evaluation study are presented here.

### Acknowledgments

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# FOOD ANALYSIS

## O-FA1

# DETERMINATION OF INTACT GLUCOSINOLATES IN BEE POLLEN BY USING ULTRA-HIGH PERFORMANCE LIQUID CHROMATOGRAPHY COUPLED TO A QUADRUPOLE TIME-OF-FLIGHT MASS DETECTOR

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In the information age in which we live, more and more research is emerging to find new compounds, which are present in foods, that can provide benefits for our health. In particular, the high number of publications concerning bee pollen analysis in the last decade demonstrates the rediscovery of this product due mainly to its associated biological activities (antimicrobial, anti-mutagenic, antioxidant...). According to the number of publications, phenolic compounds, proteins, vitamins, and carbohydrates could be considered the most representative bioactive compounds of bee pollen.

However, in the last few years, attention has also been drawn to a family of compounds, namely, glucosinolates, which are plant secondary metabolites and they are also becoming significant for human nutrition due to their preventive role in health, chiefly in terms of their breakdown products. Both the quality and the number of glucosinolates differ among plant species and subsequently in their pollen. As a result, monitoring glucosinolate content in bee pollen could be of great interest not only from a nutritional but also from a botanical point of view, as such compounds could be used as biomarkers to identify the origin of the samples.

In this study, an ultra-high performance liquid chromatograph coupled to a mass spectrometer with a quadrupole-time of flight analyzer was employed for the determination of fifteen glucosinolates in bee pollen samples for different apiaries located in Marchamalo. The proposed sample treatment involved a solid-liquid extraction with ultrapure water at 70°C followed by a solid phase extraction with cartridges containing a weak anion exchange sorbent (NH<sub>2</sub>) to achieve an efficient extraction of analytes. The chromatographic separation was carried out in gradient elution mode with a Luna Omega C<sub>18</sub> column and a mobile phase composed of a mixture of acetonitrile (0.1% formic acid) and water (0.1% formic acid) at a flow-rate of 0.2 mL/min.

Finally, the analytical performance of the proposed method was evaluated and then applied to determine the intact glucosinolates in bee pollen samples. GSLs residues have been found in most of the samples analyzed, although these differ in the number of GSLs present and their concentration.

Only one of the glucosinolates under study (glucoiberin) was not detected in any of the analyzed samples.

### Acknowledgements

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## O-FA2

### New solvents for bioactive compounds extraction from blueberry leaves

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Traditional methods for the extraction of natural products from biomass have as the main drawback the consumption of large volumes of organic solvents, which are harmful to the environment and human health [1]. In this work, we have developed an environmentally friendly method for the extraction of phenolic compounds with antioxidant activity from industrial agri-food waste subproducts, such as blueberry leaves, using natural deep eutectic solvents (NADES). This study contributes to the sustainable valorization of blueberry leaves and fulfill the main objective of the Circular Economy, maintaining the value of the products as long as possible.

In the present study, eighteen NADES were tested for the recovery of phenolic compounds present in blueberry leaves, whose extraction efficiency was evaluated by measuring total polyphenol content and antioxidant activity, and compared with that obtained with a conventional solvent (MeOH:H<sub>2</sub>O, 80:20). In most cases, the extraction yields provided by NADES were superior to the organic solvent used as a reference. In addition, the relationship between viscosity and extraction efficacy was evaluated, resulting in higher efficiency as the viscosity of the extractant decreases. Once selected and characterized the NADES with better results (ChCl:Ox, 1:1; and La:AcNa:W, 3:1:2), and in order to determine the optimal extraction conditions, the effect of factors such as temperature, time, and solid/liquid ratio on the extraction efficiency was studied using a Box-Behnken experimental design and subsequent ANOVA analysis. Optimal extraction conditions resulted to be 65 °C for the extraction temperature and 45 min for the extraction time for both NADES, whereas the optimal solid/liquid ratio was 75 for ChCl:Ox and 38 for La:AcNa:W.

In conclusion, NADES are a sustainable alternative for the recovery of phenolic compounds from agricultural by-products, thus influencing the concept of Green Chemistry. The procedure developed in this work could be applied to other residues from the agricultural industry, such as the strawberry extrudate and other red fruits [2], as well as pruning residues. It would be also applied to the extraction of bioactive compounds from food matrices such as honeys, oils, and berries.

#### Acknowledgements

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## O-FA3

# BEYOND THE ESTABLISHED LIMIT: CAPILLARY GEL ELECTROPHORESIS OF HUMAN IMMUNOGLOBULIN A FROM SERUM AND COLOSTRUM

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Breastmilk is the best feeding for newborn, especially for the preterm, infants. Human milk (HM) provides, among other bioactive products, immunoglobulins (Igs) which help to mature and improve the infant immune system. Among Igs, a key role in human milk is known to be played by immunoglobulin A (IgA). When breast feeding is not possible, for example for babies in neonatal intensive care units, the best alternative is the expressed breastmilk stored and handled in Human Milk Banks. Thermal treatment and cold storage of HM, which are necessary to ensure microbiological quality of milk, may alter its immunological factors.

Study of effect of different thermal treatment and storage conditions on IgA in human milk has been usually performed by immunoassays. These types of analysis provide information about the total amount of IgA but do not discriminate between native IgA and potential alterations, such as fragmentation and aggregation.

Capillary gel electrophoresis (CGE) is the CE mode of choice to analyze protein aggregates and fragments. The commercial kits are designed to analyze polymers up to 225 kDa.

Ig A is a very heterogeneous glycoprotein. In serum it exists mainly in monomeric form of molecular weight (MW) about 160 kDa. In milk and colostrum, secretory IgA (sIgA) of 385 kDa is the predominant form.

The objective of this work is to develop CGE methods which allow analyzing monomeric and secretory forms of IgA as well as their potential fragments and aggregates.

To optimize a method which allows going beyond the MW limit of the commercial kit, making possible to analyze forms of the protein much larger than that established limit, the effect of modifying several factors on separation of IgA forms of different size was studied.

Results showed the influence of temperature and SDS concentration on sample treatment, as well as the effect of several parameters concerning electrophoretic separation (temperature, gel-buffer dilution, injection time, injection mode, effective separation length, and gel-buffer composition). Separation of monomeric and secretory IgA and peaks potentially corresponding to fragments (< 160 kDa) and aggregates (> 385 kDa) was achieved.

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## O-FA4

# A LABEL-FREE SHOTGUN PROTEOMICS APPROACH FOR THE CHARACTERIZATION- AND DIFFERENTIATION OF QUINOA SEED VARIETIES

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Quinoa (*Chenopodium quinoa* Willd.) is a pseudocereal traditionally consumed by Andean cultures that, due to its high protein content and its balanced amino acid profile, is attracting attention worldwide as a whole grain or flour and promising source for the development of functional foods and nutraceutical products [1,2]. Despite the importance of quinoa proteins in human nutrition, biomedicine, cultivar identification, quality control and authentication, studies focused on the characterization of the quinoa seed proteome are scarce [3, 4].

In this study, proteins from seeds of black, red, white quinoa from Peru and white quinoa from Bolivia (also referred to as royal) were extracted, trypsinized in-solution, and label-free peptides were analyzed by state-of-the-art liquid chromatography-Orbitrap tandem mass spectrometry (LC-MS/MS). The raw mass spectra data searched against a specific quinoa database from The National Center for Biotechnology Information (NCBI) allowed the identification of 1,211 quinoa proteins after applying the MaxQuant/Andromeda environment. Inspection and visualization using Venn diagrams, heat maps and Gene Ontology (GO) classification graphs, revealed similarities and differences at the proteome level between the four quinoa varieties.

These results provide the most comprehensive experimental quinoa proteomic map existing to date in the literature [4], which could be used for more specific nutritional studies based on the identified proteins. Moreover, proteomic profiling of quinoa seeds could be used for quality control of quinoa and quinoa-containing foodstuff, and may pave the way to the improvement of the quinoa seed nutritional value through the optimization of industrial processing procedures or cultivar yield under different agroecological conditions.

### Acknowledgements

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## O-FA5

# Comprehensive analysis of odour-active wine volatiles by heart-cutting bidimensional gas chromatography coupled to mass spectrometry and flame ionization detection

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Instrumentally imitating human olfaction is a goal in the field of aroma study. In the case of wine this is a powerful challenge, since it is a very complex matrix where many different odorants can play a role in wine's quality. As there are different sources for these compounds, such as grapes, fermentation, oxidation or aging, odour-active volatiles belong to different chemical families and span over a wide range of concentrations; from levels over 100 mg·L<sup>-1</sup> (isoamyl alcohol) to levels well below 0.1 µg·L<sup>-1</sup> (rotundone, methoxypyrazines)<sup>[1-3]</sup>. In the present work it is explored the use of TD-GC-FID-GC-MS system with Stir Bar Sorptive Extraction (SBSE) as sample preparation strategy for a comprehensive analysis of wine odour-active odorants. The FID detection in the first dimension is used to quantify odorants present at large concentration, and the MS detector in the second dimension for the rest of them. The SBSE extraction, carried out on a strongly diluted wine matrix, makes it possible to guarantee simplicity, low matrix interference, robustness and a high degree of automation. In the final developed method, two 200 µL-aliquots of wine, equally diluted to 2 mL with a buffer-saline solution (pH 3.5, 200 g·L<sup>-1</sup> NaCl), are extracted with a SBSE (20 mm length x 1 mm PDMS film thickness) for 60 min at 500 rpm. The two twistors are further loaded independently on the autosampler and desorbed at 300°C for 15 min, concentrated in the internal focussing trap of the TD and desorbed at 300°C. Two separated injection with the same chromatographic conditions (but different heart-cuts to the second column) are required to quantify coeluted odorants. The method makes it possible in 4 hours of GC-MS to quantify compounds ranging from 1 ng·L<sup>-1</sup> (rotundone) to 300 mg·L<sup>-1</sup> (isoamyl alcohol). The final figures of merit of the method demonstrates that up to 86 odour-active compounds of wine can be satisfactorily quantified, and that 13 more, can be semiquantified. Detection limits goes from 1 ng·L<sup>-1</sup> to 1 mg·L<sup>-1</sup>, with high linearity (R<sup>2</sup>>0.99) and good repeatability (RSD<15% for 62 compounds). Overall, the method provides the most comprehensive quantification of odour-active volatiles ever reported but has limitations in the quantification of highly polar-little odorants, such as acetaldehyde or acetic acid.

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# OY-FA1

## FAST NON-AQUEOUS CAPILLARY ELECTROPHORESIS–MASS SPECTROMETRY: AN EFFICIENT ALTERNATIVE TO DETERMINE EMERGING MYCOTOXINS IN FOOD

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Mycotoxins are toxic secondary metabolites produced by some fungi that present different levels of toxicity, some of them being carcinogenic [1]. Among them, emerging mycotoxins (with possible toxicological effects, but still not included in legislation) as enniatins (ENN) and beauvericin (BEA), are getting more and more interest. Their determination requires their separation and confirmation against other compounds typically present in food, mainly in cereal samples, usually accomplished by liquid chromatography (LC) coupled to tandem mass spectrometry (MS/MS) [2].

Despite the lack of easily ionizable groups, the ionophoric character of these compounds makes them compatible with capillary electrophoresis (CE) separation. Due to their non-polar nature, a non-aqueous CE (NACE) method coupled to quadrupole time-of-flight–MS has been proposed for the first time to identify and quantify these mycotoxins.

A QuEChERS-based extraction was used as sample treatment. Separation of four ENNs (enniatin B, B1, A1 y A) and BEA was achieved in 4 min, using 40 mM ammonium acetate in 80:20 (v/v) acetonitrile-methanol as background electrolyte. “All Ions” acquisition mode (collision energies: 0 and 40 V) was selected as it allows the quantification of the main ENNs (with available standards), and the identification of unusual ENNs (no standards available).

Higher selectivity can be achieved when comparing CE with LC due to the formation of exclusive adducts such as  $[M+CH_3CH_2NH_3]^+$ . The method was validated for wheat samples, obtaining limits of quantification between 5 and 10  $\mu\text{g}/\text{kg}$ , recovery values  $>87.3\%$ , and intra- and inter-day precision values (RSDs)  $<15.2\%$  for the four ENNs and BEA. These results show the suitability of NACE-QToF-MS as an alternative for the determination of these compounds.

Finally, the method was applied to 29 wheat samples, finding 25 positives for ENN B (16-1480  $\mu\text{g}/\text{kg}$ ), 19 for ENN B1 (20-550  $\mu\text{g}/\text{kg}$ ), 7 for ENN A (10-55  $\mu\text{g}/\text{kg}$ ), 4 for ENN A1 (13-77  $\mu\text{g}/\text{kg}$ ) and 4 for BEA (12-16  $\mu\text{g}/\text{kg}$ ). Moreover, two ENNs (ENN B2 y B3) were identified in wheat.

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## OY-FA2

# DIFFERENTIATION OF TWO INDUSTRIAL HEMP VARIETIES BY COMPREHENSIVE TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY (LCxLC)

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The legalization of the industrial hemp inflorescences (*Cannabis sativa*) has increased the use of cannabis in several important files like food, cosmetic and pharmaceutical industries. The main different of these *Cannabis sativa* species in comparison to conventional marihuana is their lower concentration in psychoactive substances like  $\Delta^9$ -Tetrahydrocannabinol (THC) (<0.2-0.3%). In contrast, these species present higher concentration of cannabinoids, which are gaining interest due to their potential therapeutical effect against anxiety, stress, epilepsy or even cancer.

In terms of chemical composition, there are more than 150 cannabinoids described in hemp, but besides of these distinctive compounds, hemp contains other interesting secondary metabolites like phenolic compounds, terpenoids, and stilbenoids which contribute also to the potential functional activity of the hemp varieties. For the chemical characterization of this kind of complex samples, comprehensive two-dimensional liquid chromatography (LCxLC) is an attractive analytical tool to provide the maximum separation power that allows identifying and discovering all the interesting compounds that form the hemp metabolite profile.

In this work, two commercial and industrial Indica dominant hybrid strain hems (THC content <0.2%) have been analyzed by LCxLC coupled to HRMS to evaluate their individual cannabinoid and secondary metabolite profile. These varieties are recognized and differentiated by their organoleptic properties that can be related to their metabolite composition. Therefore, the objective of this study was to evaluate the metabolic profile of the two Indica hybrids to determine possible differences in the chemical composition that can affect the biological activity and can be of interest for different industrial applications.

## WC-FA1

# Evaluation of the degradation of tropane and opium alkaloids in baked breadstick samples

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Tropane alkaloids (TAs) are secondary metabolites produced by a variety of plants, including *Datura stramonium* L (jimsonweed). Atropine and scopolamine are the best-known representative TAs. These alkaloids can contaminate foods when TAs-producing plants (seeds, leaves, etc.) are harvested together with crops of cereals, pseudo-cereals, legumes, etc. [1]. Poppy seeds are obtained from the opium poppy (*Papaver somniferum* L.). The latex (milky sap) of the opium poppy contains different alkaloids, such as morphine, codeine, noscapine, thebaine and papaverine. Mature poppy seeds become contaminated with opium alkaloids (OAs) as a result of pest damage and during harvesting [2]. Despite studies focused on TAs and OAs contamination, there are few studies that evaluate how these compounds may be affected by baking conditions. As the consumption of products made from cereal flours and poppy seeds is increasing, it is important to study the degradation during processing to assess the actual intake of these alkaloids as recommended by EFSA.

In this work, the degradation of TAs and OAs was studied in samples of breadsticks prepared with corn flour, contaminated with jimsonweed seeds, and poppy seeds in different proportions and thermal processing conditions. The compounds were extracted by solid-liquid extraction with methanol containing 0.1% acetic acid followed by a step of evaporation and reconstitution in Milli-Q Water with 0.1% trifluoroacetic acid (preconcentration factor of five) prior to analysis by a HPLC-DAD chromatographic method. The separation of the eight alkaloids was performed with an InfinityLab Poroshell 120 EC-C18 column (3.0 x 150mm, 2.7 µm) employing a mixture of Milli-Q Water with 0.1% trifluoroacetic acid and acetonitrile as mobile phase in gradient elution mode at a flow rate of 1 mL/min and 30°C with a total analysis time of 12 minutes. Detection was performed at 212 nm (morphine, codeine, anisodamine, scopolamine, atropine and noscapine), 225 nm (thebaine) and 240 nm (papaverine). This method has been optimised and validated, obtaining recovery values between 92 and 99%, so it can be applied to real samples.

Breadsticks samples doped with stramonium seed powder (0.1 and 1% add in corn flour) and poppy seeds (5 and 10%) in the kneading and baked at 180°C for 20min shown a degradation of atropine around 97%, morphine between 57 and 91% and noscapine between 44 and 74%. But, despite degradation, there are appreciable amounts of atropine (3 mg/100g), morphine (0.43-0.98 mg/100g) and noscapine (0.17-0.28 mg/100g) in the samples of breadsticks doped with 0.1% stramonium seed powder and 5% poppy seeds.

### Acknowledgements

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## WC-FA2

# DERIVATIZATION/EXTRACTION OF RELEVANT THIOLS IN WINE AND ANALYSIS BY STABLE ISOTOPE DILUTION ASSAY AND UHPLC-MS/MS. A SIMPLE PROCEDURE TO ACHIEVE LOQ BELOW THE SENSORY THRESHOLD

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The polyfunctional thiols 4-mercapto-4methylpentan-2-one (4-MMP), 3-mercaptohexanol (3-MH), 3-mercaptohexyl acetate (3-MHA), benzyl mercaptan (BM), and 2-furfurylthiol (FT) are potent odorants in wine with low sensory thresholds: 0.8, 60, 4.0, 0.3, and 0.4 ng/L, respectively. In addition, their high reactivity and poor spectrometric properties make it necessary to perform a derivatization step prior to their analysis either by GC [1] or LC [2].

A fast sample preparation consisting of a simultaneous derivatization/extraction with a selenium-containing reagent (2-phenyl-1,2-benzisoselenazol-3(2H)-one, Ebselen) and dichloromethane in a 1-min vortex agitation at room temperature under anoxic conditions yields a selenyl-sulfide derivative through the formation of a Se-S bond as reported Vicchi et al. [3]. Selective mass fragmentations yields for all derivatives  $[C_{13}H_{10}ONSe]^+$ ,  $m/z$  276 as the selenyl moiety coming from the breakup of the selenyl-sulfide bond formed in the derivatization/extraction step. In order to avoid additional sample preparation or cleanup steps, the use of commercially available deuterated analogs is the simplest and most efficient way to correct the recoveries, compensate for any possible matrix effects and achieve the best repeatability.

The proposed method allowed quantifying the above mentioned polyfunctional thiols employing a simple sample preparation and a chromatographic run of only 17 min. LOD for 4-MMP, 3-MH, 3-MHA, BM and FT were 0.020, 0.002, 0.046, 0.061, 0.028 ng/L while LOQ were 0.066, 0.006, 0.154, 0.203, and 0.093 ng/L, respectively. Linearity in the studied linear range with six calibration points showed satisfactory results with  $R^2 \geq 0.992$  for all compounds. Repeatability studies were performed by analyzing triplicates of 4 wines (2 reds and 2 whites) spiked with the compounds under study. In all cases, %RSD was below 10%, being in most cases less than 6%. Finally, matrix effects were considered negligible as the slopes in real wine vs. model wine did not show significant differences.

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## WC-FA3

# DETERMINATION OF AMINO ACIDS IN BEE POLLEN BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY COUPLED TO A FLUORESCENCE DETECTOR

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One of the hive products that is currently attracting more attention is bee pollen. This is due to its multiple positive health properties, making it a very popular food supplement. It contains a large number of bioactive compounds, such as fatty acids, vitamins, minerals, proteins and amino acids. The protein content is especially important, which is one of the two factors that mainly determines the nutritional value of pollen. The second factor is the concentration of amino acids and specifically essential amino acids. In fact, bee pollen is the only known food that contains all 20 encodable protein amino acids.

Therefore, the main objective of this work is to determine the content of free amino acids present in bee pollen samples collected by *Apis mellifera* L. bees from different hives in the province of Guadalajara (Spain) using high performance liquid chromatography operating in reverse phase mode (C<sub>18</sub>-based column) and with a fluorescence detector. It will be necessary to perform a pre-column derivatization of the amino acids using two reagents: o-phthalaldehyde and 9-fluorenylmethyl chloroformate. The sample treatment comprises of an amino acid extraction with ultrapure water, a homogenization with an Ultra-Turrax® that will be followed by a centrifugation of the extract, and the collection of the supernatant. This procedure is repeated, the supernatants are combined and further diluted with ultrapure water. Finally, the analytical performance of the proposed method was evaluated and then applied to determine the amino acid content in the different samples, with most of the amino acids studied being present in all of them. The predominant amino acid in all samples is proline.

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## WC-FA4

### Occurrence of emerging pollutants included in the new EU Drinking Water Directive (DWD) (2020/2184) in tap water from Barcelona metropolitan Area

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The aim of this study is to provide a broad description of occurrence for emerging pollutants (chlorate, chlorite, haloacetic acids, bisphenol A, per- and polyfluoroalkyl substances) included in the new EU Drinking Water Directive (DWD) (2020/2184) [1].

The applied disinfectants in water potabilization process can react with the natural organic matter and anthropogenic contaminants present in the water to form disinfection by-products (DBPs). Formation of DBPs is a current global concern due to their potential relation to chronic diseases. Chlorate, chlorite and haloacetic acids (HAAs) are the DBPs we assessed in this study.

Bisphenol A (BPA), is often used to synthesize polymer materials (e.g., polycarbonates and epoxy resins) and also used to produce fine chemical products, such as plasticizers, flame retardants, thermal stabilizers and rubber antioxidants. BPA is an endocrine disruptor and has harmful estrogenic activity for humans and aquatic organisms [2].

Per- and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals widely used in industrial and commercial applications as water and oil repellents, fire retardants, herbicide and insecticide formulations, cosmetics, greases and lubricants, paints, polishes and adhesives. PFAS are water-soluble chemical compounds of concern due to the environmental persistence, biomagnification in food webs, long-distance transport, as well as their potential accumulation and toxicity. Drinking water is one of the main routes of human exposure to PFAS.

We quantified these compounds in 53 drinking water samples sourced from Barcelona metropolitan area: tap water (N=42, one per postal code) and tap water after filtered using household water filter of activated carbon (N=6) or reverse osmosis (N=5). Chlorate, chlorite, PFAS and HAAs were analyzed by Liquid Chromatography-Electrospray Ionization-Tandem Mass Spectrometry (LC-ESI-MS/MS) and BPA by Gas Chromatography-Mass Spectrometry (GC-MS) [3, 4]. The concentration levels ranged between <10-367, <10-149, <LOQ-34.9 and <LOQ-0.18 µg/L for chlorate, chlorite, total values of HAAs and PFAS, respectively. On the other hand, BPA was not detected in any of the samples above the quantitation limit. No concentration exceeds the parametric values regulated in the DWD (2020/2184).

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# WC-FA5

## OPTIMIZATION OF A SPME GC-MS APPROACH FOR AUTHENTICATION OF MATCHA TEA

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The consumption of tea (*Camellia sinensis*) infusions, deeply ingrained in Asian culture, has experienced a noticeable growth in West countries, favored by the great diversity of varieties currently available (green, black, white, oolong, etc.). Among them, matcha tea, which is a non-fermented green tea with a singular processing, is highly appreciated worldwide [1]. Its relatively high economic value, associated with its unique organoleptic properties and health benefits [2], make matcha tea frequently the object of fraudulent practices. Therefore, the development of improved analytical methodologies to authenticate matcha tea is a topic of wide interest, not only for trading companies, but also for regulatory bodies.

In this work, a Solid-Phase Microextraction Gas Chromatography-Mass Spectrometry (SPME GC-MS) method has been optimized and further applied to the analysis of 18 commercial green/matcha teas and to a number of laboratory-made adulteration of matcha tea with green tea (in the range 95:5-50:50, w/w) in the search for authenticity markers.

Under optimal SPME operating conditions (DVB/CAR/PDMS fiber, 0.5 g, T=60°C,  $t_{eq} = t_{ext} = 15$  min, 2 min splitless), more than 90 volatiles (aldehydes, alcohols, terpenoids, etc.) were identified, with 1-penten-3-ol, hexanal and 6-methyl-5-hepten-2-one showing the highest relative concentration (%) irrespective of the green tea sample considered.

Principal Component Analysis of quantitative data evidenced a wide intra-group variability and a number of green tea/matcha tea samples with a very distinctive volatile profile. As for the Stepwise Discriminant Analysis of data, 2-ethyl-furan,  $\alpha$ -ionone and tetrahydro-trimethyl-2(4H)-benzofuranone were shown as the most significant ( $F > 16$ ) variables for differentiation of green tea and matcha tea (100% correct classification). Although some extent of clustering was found, particularly for matcha teas, it was not correlated with their declared quality. ANOVA analysis of these discriminant variables made also possible the identification of additions of 5-20% green tea in laboratory-made adulterated matcha tea samples.

To conclude, the SPME GC-MS methodology here optimized is shown as a green, fast and affordable approach that can be easily implemented for volatile profiling of green tea samples and for the intended proposal of green tea/matcha tea authenticity markers.

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## WC-FA6

# ANTIOXIDANT CAPACITY OF GARLIC (*ALLIUM SATIVUM L.*) EXTRACT FROM THE NORTH-CENTRAL REGION OF MEXICO

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Garlic contains organosulfur compounds and polyphenols, to which various health-promoting effects and antioxidant properties are attributed. The aim of this study was to estimate the antioxidant capacity *in vitro* of “Jaspeado” garlic (*A. sativum L.*), bulbs collected from the north-central region of Mexico were used for extraction and analysis by means of spectrophotometric techniques. The extractions were carried out by maceration with PBS, methanol, ethanol. The total polyphenol content was determined using the Folin Ciocalteu colorimetric assay. While the antioxidant properties were evaluated by DPPH and ABTS. The total polyphenolic content varied from 6.9 to 70 mg EAG / g of macerated garlic; the highest yield was achieved with 50/50 EtOH/PBS. The DPPH assay in all extracts exhibited antioxidant activity ranging between 4 and 222.3 mM of Trolox per g of garlic, especially high in PBS (100%). ABTS showed variations in comparison with DPPH since the highest antioxidant capacity was registered when the maceration was carried out with 50/50 EtOH/PBS giving a yield of 152.67 mM of Trolox per g of garlic. The garlic extracts showed antioxidant activity demonstrable, the highest activity and amount of total polyphenols and antioxidant capacity were observed on 50/50 EtOH/PBS extract, while for DPPH, PBS extract revealed greater antioxidant activity.

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## WC-FA7

# Optimization of ultrasound-assisted extraction via ultrasound bath and sonotrode of phenolic compounds with high antioxidant activity from mango seed

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Mango seed is one of the main by-products from mango juice industry. It is a known source of bioactive compounds, mostly phenolic compounds, and it has been widely studied for its antimicrobial, antioxidant, anti-cancer, cardioprotective and neuroprotective activities, among others [1]. Ultrasonic-assisted extraction (UAE) is an extraction technique frequently used for the isolation of phenolic compounds in food [2] and its by-products [3]. Thus, this research focuses on the establishment of UAE conditions to obtain phenolic compounds in mango seed by ultrasonic bath and sonotrode. For this purpose, two Box–Behnken designs were carried out. The ultrasonic bath experimental design was composed of 15 experiments and three independent factors: Ratio sample/solvent (1:25-1:75-1:125 w/v), ratio ethanol/water (40:60-70:30-100:0 v/v), time (10-50-90 min), and the sonotrode experimental design was of 27 experiments and four independent factors: Ratio sample/solvent (1:50-1:775-1:1500 w/v), ratio ethanol/water (30:70-65:35-100:0 v/v), time (5-25-45 min) and amplitude (20-60-100 %). In both models the responses were phenolic compounds measured by Folin-Ciocalteu and the antioxidant activity measured by ABTS, FRAP and DPPH. The validity of the experimental designs was confirmed by ANOVA and the optimal extraction conditions were obtained by response surface methodology: 1:90 ratio sample/solvent (w/v), 60:40 ratio ethanol/water (v/v) and 60 min for ultrasonic bath UAE and 1:1400 ratio sample/solvent (w/v), 60:40 ethanol/water (v/v), 30 min and 70% amplitude for sonotrode UAE. The extracts obtained with the optimal conditions were analyzed by High Performance Liquid Chromatography coupled to mass spectrometer detector (HPLC-ESI-TOF-MS) and 39 polar compounds were identified: thirty-one phenolic acids, six flavonoids and two organic acids. According to the results, the UAE with sonotrode has demonstrated to be better as let obtain up to 60% higher amount of phenolic compounds (with higher antioxidant activity than UAE with bath).

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# WC-FA8

## ESTABLISHMENT OF ULTRASOUND-ASSISTED EXTRACTION VIA SONOTRODE BY BOX-BEHNKEN METHODOLOGY TO OBTAIN HIGH PHENOLIC RECOVERY FROM CHERIMOYA LEAVES

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Leaves of *Annona cherimola* Mill. (Cherimoya) are a potential source of bioactive compounds and are currently used as ingredients in food supplements as well as in the teas elaboration for the treatment of gastric, intestinal, cardiovascular, skin, and eye diseases [1,2]. These beneficial properties are attributed mainly to their phenolic composition. However, literature on phenolic extraction in cherimoya leaves is scarce, thus this research focused on the investigation of the set-up of ultrasound-assisted extraction via sonotrode of phenolic compounds in cherimoya leaves. To establish the sonotrode extraction, a Box-Behnken design based on response surface methodology (RSM) was used to optimize the effects of factors such as amplitude (20-100%), extraction time (1-20 min) and solvent composition (0-100% EtOH). Qualitative and quantitative analyses of phenolic compounds were performed using HPLC-ESI-TOF-MS. A total of 26 phenolic compounds were identified in cherimoya leaf extracts. The highest content of phenolic compounds was  $12.1 \pm 0.6$  mg/g d.w. obtained at 70% amplitude, 10 min and 40:60 EtOH/H<sub>2</sub>O (v/v). This value was 1.82 times higher than the obtained by a conventional ultrasonic bath at 80:20 EtOH/H<sub>2</sub>O (v/v) and 20 minutes ( $6.6 \pm 0.2$  mg/g d.w.). Therefore, sonotrode could be considered as an efficient extraction technique that allows a good recovery of phenolic substances from cherimoya leaf that could be easily scale-up at industrial level. Moreover, it has been evaluated the antioxidant activity by FRAP, ABTS and DPPH assays of the optimal cherimoya extract.

### Acknowledgements

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## WC-FA9

# Design of a microfluidic paper-based device for the quantification of phenolic compounds in wines

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Nowadays, the focus of Analytical Chemistry on miniaturization aims mainly to minimize sample and reagents volumes, together with reduction of waste generation. In this context, microfluidic paper-based analytical device ( $\mu$ PAD) have been gaining popularity from its first appearance in 2007 by Martinez A et al. [1]. This has been mainly due to the well-known features of  $\mu$ PADs, namely portability and low cost production combining (in most cases) with Green Analytical Chemistry approach.

Wine is one of the most consumed alcoholic beverages in the world and it represents an important economic industry. Among other wine constituents, polyphenols are a group of natural compounds present in both, grapes and wines, that have been reported as human beneficial and crucial in the organoleptic properties of the final wine [2]. As a result, total polyphenol content (TPC) monitoring has become a common practice in wines in order to control the quality as well as detect frauds with lower quality products (ca. authentication purposes).

In this context, we report the design and development of a new microfluidic device for for the quantification TPC in wines using the known Folin-Ciocalteu colorimetric reaction and a novel approach of  $\mu$ PAD fabrication [3]. This method aimed to be an easy alternative for the real time determination of TPC in wines wine any sample pretreatment steps except a dilution. Two phenolic compounds (gallic acid and taniraisin) were selected as solute test in these samples. In the  $\mu$ PAD assembly, parameters such as reagents, type of paper, sample volumes, among others, were optimized. Furthermore, analytical features of interest from the developed  $\mu$ PAD were established and the method was successfully applied to 10 real samples including sparkling and table wines.

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## WC-FA10

# Determination of phenolic compounds in artisanal água-mel produced on the South of Portugal

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Água-mel is a sub-product originating from the honey industry produced with residues of honey, pollen and bees wax. Briefly, it is obtained by scalding previously crumbled honeycombs (wax from the bee hives) with water and squeezing the remaining honey residues and also pollen out and Alentejo and Algarve (Portugal) [1,2,3].

In the present study, a total of 20 água-mel samples were purchased from traditional producer in the Algarve (E) and Alentejo (O) regions. Extraction of phenolic compounds from água-mel samples was based in method described by Karabagias et al 2014 with modifications. An Agilent 1200 series ultrahigh-performance liquid chromatography system (Agilent Technologies, Santa Clara, CA), was employed for targeted metabolomic analysis of strawberry extracts. The column used was a 50 mm × 2.1 mm i.d., 1.8 µm, Zorbax SB-C18 (Agilent Technologies, Santa Clara, CA), thermostated at 30 °C. Optimum separation was achieved using a binary gradient delivered at 0.4 mL/min flow rate, consisting of 0.2% acetic acid in water (v/v) at pH 3.10 (solvent A) and pure acetonitrile (solvent B). The eluent from the column was directly introduced into a model 6410 triple quadrupole mass spectrometer equipped with an electrospray ionization source (ESI) and controlled by Mass Hunter Workstation Software (Agilent Technologies, Santa Clara, CA). Source working conditions were capillary voltage 4000 V, gas flow rate 10 L/min, gas temperature 300 °C, and nebulizer pressure 35 psi. Phenolic acids, flavonoids, ellagitannins, and ellagic acid derivatives were detected in the negative ion mode. Detection was performed in dynamic multiple reaction monitoring (dMRM) mode using retention times and detection windows, which improves chromatographic peaks and provides increased reproducibility and accuracy of quantitation. Twenty one compounds (Gallic acid, Gallic acid, 4- Hydrobenzoic acid, Tirosol, Tirosol, Vainilic acid, Chlorogenic acid, Catequin, Caffeic acid, Seringic acid, Vanilin, p-coumaric acid, Benzoic acid, Ferrulic acid, Sinapic acid, Epicatechin, Rutin, Quercetin-3- glucoside, Hesperidin, Quercetrin, Revesterol and Cinnamic acid) were identified in água-mel samples.

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## WC-FA11

# DEVELOPMENT OF A MULTI-CLASS METHOD FOR MONITORING PESTICIDE RESIDUES IN CEREALS MARKETED IN THE CANARY ISLANDS

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Despite the introduction of ultra-processed foods into society, cereals continue to be a staple of diet of the Canarian population, especially *gofio*, which is originally produced in the Archipelago. In this sense, the high demand of the islanders, as well as the decrease in the own production due to the urban development, have given rise to a huge import of maize, wheat, among other cereals from the Iberian Peninsula, France and Argentina [1]. The worldwide agricultural production would be unreachable without the use of phytosanitary products that protect crops from pests, but at the same time, this action generates the need to monitor the pesticide residues levels in the final products to guarantee their safe consumption.

Therefore, in the present work, an analytical methodology was developed to evaluate the presence of a wide variety of pesticides in oat, rye, spelt and quinoa matrices using the QuEChERS extraction method [2]. The selection of the samples was carried out considering the increase in the consumption of these cereals and pseudo-cereals in the last years due to their high nutritional values. An ultra-high performance liquid chromatography system coupled to a mass spectrometry detector with single quadrupole-time of flight as analyzer were used for the separation and determination of target analytes, respectively. Finally, the method was thoroughly validated following the European guidelines of SANTE/12682/2019 guide [3] achieving good recovery values (with relative standard deviations lower than 20%) and high sensitivity that ensures the reliability of the analytical results.

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## WC-FA12

### FOOD SAFETY EVALUATION OF COMMERCIALY AVAILABLE DAIRY PRODUCTS

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The growth of food industry and the development of global food market make necessary the application of strict controls on the security and quality of food products consumed by population. Especially sensitive is the safety of food intended for infants such as dairy products since certain compounds present in this kind of matrices have important negative effect on human health, and particularly in this vulnerable group. Indeed, such substances can act as endocrine disruptors producing numerous hormonal diseases, including the development of diverse types of cancer [1].

Considering the transcendence of all above mentioned, the application of reliable analytical methodologies that allow the monitoring of hazardous substances such as endocrine disrupting compounds has great interest to guarantee food safety and extend the knowledge about the influence of this kind of compounds on consumers health. In that case, the use of QuEChERS method as extraction and clean-up strategy and subsequent determination using ultra-high performance liquid chromatography-tandem mass spectrometry has been chosen for the analysis of a wide group of endocrine disruptors including natural and synthetic estrogens, mycoestrogens and phytoestrogens in dairy products [1,2].

Results showed the occurrence of several phytoestrogens in different products commercialized in Spain and widely consumed by the population. Especially worrisome is the detection of such compounds in some of the evaluated products intended for infant population. This data comes up with the necessity of developing further studies in this area that provide authorities more accurate and reliable information to establish adequate restrictive guidelines about the presence of such compounds in food products.

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**EVALUATION OF QUALITY OF *Plectranthus barbatus* FOOD SUPPLEMENTS BY CHROMATOGRAPHIC TECHNIQUES COUPLED TO MASS SPECTROMETRY.**

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*Plectranthus barbatus* (also known as *Coleus forskohlii*) is a perennial plant from the Lamiaceae family widely used in traditional Indian medicine (Ayurveda), due to its antioxidant, analgesic and anti-inflammatory properties, etc. Among other compounds, roots of *P. barbatus* are rich in bioactive labdane-type diterpenoids, mainly forskolin. This diterpenoid has been shown to induce lipolysis of adipocytes and to promote the loss of fat cells, thus presenting beneficial effects for weight control. Consequently, the consumption of food supplements (FS) with high content of forskolin to treat disorders as obesity has increased in the last years. However, FS are not subject to a strict legal framework like prescription drugs are. Therefore, FS manufacturers are responsible for the compliance regarding bioactive content and safety of their products.

In this work, a multi-analytical strategy based on the GC-MS and LC-MS analysis of *P. barbatus* FS has been developed to verify their quality and authenticity. Twenty four FS based on *P. barbatus* extracts were purchased through websites, while *P. barbatus* roots were acquired in herbal shops for comparison purposes. Extracts in heptane and methanol were obtained by ultrasound-assisted extraction; non-polar extracts were directly analyzed by GC-MS using a polydimethylsiloxane capillary column, while methanolic extracts were analyzed by RPLC-MS using a C18 column and by GC-MS previous derivatization.

Forskolin was successfully identified and quantified by GC-MS and LC-MS analysis in roots; however, it was only detected in 50% of the analyzed FS. Regarding forskolin concentration, 3 FS showed lower values than those declared. Other characteristic compounds of roots such as sedo-heptulose, 1,9-dideoxyforskolin, 9-deoxyforskolin and isoforskolin, were also detected in some of these FS. The combined use of GC-MS and LC-MS allowed to detect in 4 FS the substitution of the declared natural source by extracts of green tea, soy leaves and a plant of the Berberidaceae family. Low concentrations of carbohydrates similar to those present in roots were found in 3 FS, whereas only excipients such as maltodextrins were detected in the others. The proposed multi-analytical strategy was shown to be advantageous over single analytical techniques to detect frauds related to the authenticity of the natural source and the mismatch between the presence and content of declared bioactive compounds in *P. barbatus* supplements.

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# WC-FA14

## GC-MS METHODOLOGY FOR QUALITY EVALUATION OF SAFFRON FOOD SUPPLEMENTS

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Saffron (*Crocus sativus* L.) stigmas are mainly composed of crocins, picrocrocin and safranal, which are responsible for its characteristic colour, taste and aroma. These compounds, also associated with a wide range of bioactivities (antioxidant, antidepressant, anti-inflammatory, etc.) [1], have promoted the use of saffron extracts in food supplements (FS). On the other hand, saffron is the most expensive spice in the market, and one of the most adulterated. Although several analytical techniques and methodologies have been proposed to detect frauds in this spice, very few studies have addressed the evaluation of saffron supplements quality.

Saffron commercial extracts are often standardized in safranal content. However, their determination is commonly done by UV spectrometry (ISO 3632) or by HPLC-UV [2], which sometimes lack of the required selectivity. Due to the high sensitivity and resolution power of gas chromatography coupled to mass spectrometry (GC-MS), in this work, a new methodology based on this technique has been developed for the reliable determination of safranal and other compounds aimed in quality control of saffron FS.

Affron<sup>®</sup> was employed as a reference extract for optimization of the analytical procedure which was further applied to different FS. Several solvents (methanol, acetone, dichloromethane, chloroform, diethyl ether and heptane) were assayed for volatile extraction and different GC-MS experimental conditions such as column (ZB-1 and ZB-5), inlet temperature (230, 250, 280°C) and split ratio (1:10, 1:20 and 1:30) were evaluated. Furthermore, different derivatization procedures (trimethylsilylation or trimethylsilyl oximation) were assayed in order to determine the semi volatile composition.

The developed methodology allowed the determination of picrocrocin, *myo*-inositol and glycosyl-inositols in saffron FS for the first time by GC-MS. These compounds, also present in saffron stigmas, together with safranal, could be considered good markers of saffron FS authenticity. The GC-MS methodology here optimized is shown as an improved alternative to conventional HPLC-UV methods for the assessment of saffron FS quality and authenticity.

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**WC-FA15**  
**THE EFFECT OF THE ADDITION OF *HAEMATOCOCCUS PLUVIALIS* WET PASTE  
IN COLOURING AND IMPROVEMENT OF THE ORGANOLEPTIC AND NUTRITIONAL  
PROPERTIES OF *FILLOAS***

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In the food industry, there is concern about the extensive use of artificial colourants derived mainly from the petrochemical sector [1]. Moreover, in addition of providing no added value beyond colouring, these dyes can present adverse effects on health [2]. In response to these global issues, this work provides a natural colouring alternative to artificial additives, through the application of the wet paste of the microalgae *Haematococcus pluvialis* red phase, rich in astaxanthin, as a partial substitute for wheat flour (7% and 13% w/w) in the preparation of *filloas* (Galician pancakes), a typical dessert from the northwestern region of the Iberian Peninsula. To determine its capacity as a natural pigment, the stability of the colour over the time (0, 3, 6 and 9 days) was compared with a commercial dye. At the same time, to test its functionality as a food preservative, its physicochemical properties, were measured. To assess the enrichment of functional properties in the food matrix, the main bioactive compounds (carotenoids, fatty acids, and polyphenols) were quantified by UHPLC-DAD-QTOF. The results for the colouring capacity of *H. pluvialis* showed a reddening stability 8% higher than that of the artificial colourant. Within its organoleptic characteristics, the texture showed a significant response ( $p < 0.02$ ), improving its properties as the concentration of the microalgae increased, showing during the first 6 days, an extensibility of 15.10 mm and a tenacity of 3.23 N, which represents an improvement of 19% and 52% respectively in comparison with to the control group. In turn, an enrichment in the concentration of carotenoid compounds around 300  $\mu\text{g/g}$ , as well as an important presence of fatty acids and phenolic compounds, were observed. This, together with a potential to moderate microbiological degradation evidences the potential use of *H. pluvialis* as a natural food additive.

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**WC-FA16**  
**DETERMINATION OF BETAINES IN BEE POLLEN BY USING HIGH PERFORMANCE  
LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY**

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Bee pollen is a dietary supplement with numerous bioactive compounds that are beneficial to health. This bee product has been used in the human diet for many centuries, being its consumption more common every day, due to its nutritional and healthy properties. The composition of bee pollen, which includes compounds such as proteins, amino acids, lipids, phenolic compounds, vitamins, glucosinolates and betaines, depends on several factors and not only on its origin (plant species and geographical), but also on the type of soil, the weather conditions, beekeeping practices or processing prior to sale.

In this work, the betaine content in bee pollen samples from four different apiaries, which were located in Marchamalo (Guadalajara, Spain), was determined by means of liquid chromatography coupled to a single quadrupole mass detector equipped with an electrospray ionization source, which was operated in positive mode. For this purpose, an efficient and selective sample treatment has been proposed, with average analyte recoveries higher than 80% and absence of the matrix effect. This involved a solvent extraction and a further dilution of the extracts. Chromatographic analysis was performed on a hydrophilic interaction-based column. The mobile phase consisted of acetic acid (0.1%) in water and acetonitrile, with a flow-rate of 0.5 mL/min in gradient elution mode. The method was fully validated and the data demonstrated that it is consistent, reliable and has a wide linear range of applicability. Finally, the proposed method was applied to betaine analysis of the bee pollen samples from Marchamalo, and it has been observed that all samples contain betonicine, betaine, trigonelline, and choline; meanwhile, the betaine found in the highest quantity in all samples was betonicine.

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