XXIII MEETING OF THE SPANISH SOCIETY OF CHROMATOGRAPHY AND RELATED TECHNIQUES

Pamplona, 23-25 October 2024

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WELCOME

Dear colleagues and friends,

Welcome, everyone, to Pamplona and to the XXIII Meeting of the Spanish Society of Chromatography and Related Techniques (SECyTA). We are also pleased to welcome you to the School of Pharmacy and Nutrition at the Universidad de Navarra.

This event provides us with the opportunity to once again share days filled with science, collaboration, and friendship. We have organized this meeting with great enthusiasm, and the members of the Organizing and Scientific Committees are confident that it will be both interesting and stimulating for all of you.

The topics to be addressed at the conference are as follows: T1: New developments in analytical instrumentation/detection systems, T2: Fundamentals on chromatography and electro-driven separations, T3: Sample preparation methods, T4: Environmental and industrial analysis, T5: Biological, toxicological, and forensic analysis, T6: Food and nutritional analysis and T7: Chemometrics, data processing, and omics techniques.

In addition, a special session has been organized to discuss the potential, possibilities, and opportunities that Artificial Intelligence offers for chromatographic techniques.

For all of us dedicated to chromatography and related techniques, this is a chance to share our latest research and connect with national and international speakers, as well as company representatives who will present new tools to address current challenges. Additionally, we will have opportunities to discuss, ask questions, learn, and conceive new lines of research, collaborations, and projects.

A special welcome goes to our early-career researchers, who represent the future of our field. We trust that these meeting days will offer them new perspectives, ideas, and professional connections.

We extend our gratitude to the companies supporting us and to everyone who has contributed in various ways to the organization of this event.

In addition to the scientific program, we have organized social activities that will allow you to experience the city and, of course, its rich gastronomy.

For all these reasons, we hope everyone takes full advantage of and enjoys these days in Pamplona.

On behalf of the local organizing committee

Elena González Peñas and Elena Lizarraga Pérez

ORGANIZING COMMITTEE

Elena González Peñas, *Chairwoman*
Universidad de Navarra

Elena Lizarraga Pérez, *Chairwoman*
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Belén Gómara Moreno
Instituto de Química Orgánica
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José A. González Pérez
Instituto de Recursos Naturales
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(IRNASE-CSIC)

Mario Fernández Martín
Instituto de Química Orgánica
General (IQOG-CSIC)

Marta Lores Aguín
Universidad de Santiago de
Compostela

INVITED SPEAKERS

JOSÉ BERNAL DEL NOZAL

University of Valladolid

Determination of contaminants in bee products by using chromatographic techniques

José Bernal del Nozal is full Professor in Analytical Chemistry and head of TESEA group, University of Valladolid, has contributed for expanding the knowledge about some relevant issues such as food safety and quality, including the analysis of contaminants and bioactive compounds, and in development of new analytical strategies, especially those that involved green chemistry. In the last years, he has mainly worked in the apiculture area, especially in developing new strategies for determining pesticides and bioactive compounds in bee products.

During his scientific career, he has worked with several analytical separation techniques as HPLC, GC, CE and SFC. He has also contributed as author/co-author to more than 120 scientific publications (H-index of 29), 90 congress presentations, 6 book chapters, and 1 patent. In addition, he has also participated as Principal Researcher/Researcher in 17 research projects or contracts with various industries and government agencies. He is also an Associate Editor of Food Analytical Methods, and member of the Editorial Board of several journals as Journal of Food Composition and Analysis, Foods, Separations, Measurement: Food, and Molecules. Finally, he has also have supervised 4 PhD thesis, and he is currently supervising three more, and he has been also selected for the evaluation of national and international projects.

INVITED SPEAKERS

JENNIFER KIRWAN

Charité University Hospital

The metabolome and the immune system; why good chromatography matters!

Dr. Kirwan started her career as a clinical veterinarian where she became increasingly interested in translational and evidence based medicine before undertaking a PhD in metabolomics. She now heads the Berlin Institute of Health Metabolomics Platform at Charité University Hospital in Berlin, where she focuses on translational health-related metabolomics, especially on its quality management aspects. She is particularly interested in the gut-brain-heart health triad and how the microbiome influences health.

She is a founding member of the German Metabolomics Society, a Central Committee member of the international Metabolomics quality assurance and quality control consortium (MQACC) and is an active member of the Precision Medicine and Pharmacogenomics working group of the International Metabolomics Society.

INVITED SPEAKERS

GABRIEL VIVÓ-TRUYOLS

Tecnometrix

Chromatographic big data analysis using Bayesian statistics: finding alternative ways to automation

Gabriel Vivó-Truyols (1975) studied analytical chemistry at the University of Balearic Islands (Spain) and graduated in 1998. In 2004 he obtained his PhD with honours from University of Valencia (Spain) on chemometrics methods for optimization and data treatment of HPLC. His PhD dealt with the development of novel methods for optimization and data treatment in HPLC, and was awarded with the D.L. Massart award in chemometrics from the Belgian Chemometrics society in 2006, given every two years to the best PhD thesis in chemometrics, world-wide. In 2004 he joined the team of Peter Schoenmakers (University of Amsterdam), where he developed a research program focused on chemometric techniques for optimization, calibration and data-treatment of two-dimensional chromatographic methods. In 2007 he joined the analytical chemistry team at BP in Sunbury (London area). He worked as chemometric specialist developing algorithms and software for GCxGC analysis of petroleum subproducts, as well as developing chemometrics methods for on-line infra-red analysis. In 2009 he re-joined the analytical-chemistry group of Peter Schoenmakers at University of Amsterdam as assistant professor. He left in 2017, establishing his own consultancy (based in Spain) in data analysis for chromatography and spectroscopy. With 20+ years of teaching experience at 4 different universities in this subject, Gabriel is currently scientific consultant for major multinationals in the area of data analysis, including BP, Castrol, BASF, Merck and Agilent technologies, as well as a collaborator with the university of Pardubice (Holcapek group) and member of the United States Pharmacopeia (where he is chair of the chemometrics joint subcommittee). Gabriel Vivó-Truyols has co-authored more than 60 papers, besides a book (in the making) covering the interface of chemometrics & chromatography.

INVITED SPEAKERS

FREDERIC BÉEN

Vrije Universiteit and KWR Water Research Institute

Novel developments to monitor environmental contaminants and their transformation products in the aquatic environment using high-resolution mass spectrometry and data science

Dr. Frederic Béen is an Assistant Professor in the Chemistry for Environment & Health research group at the Amsterdam Institute for Environment and Health (A-LIFE) of Vrije Universiteit Amsterdam. He also serves as a Senior Scientist at KWR Water Research Institute in the Water Quality and Health research group. Frederic's work focuses on developing and enhancing suspect and non-target screening applications to monitor a wide range of environmental contaminants.

His research explores how chromatography (LC and GC) and HRMS, along with data analysis pipelines, to better understand the source, fate, and impact of contaminants on humans and the environment. This involves developing cheminformatics and data analysis tools, such as chemometrics and machine learning, to analyse large sets of chemical and mass spectrometric data. Frederic's research includes applying these techniques to human biomonitoring, effect-directed analysis (EDA), and micro- and nanoplastic analysis. He also explores wastewater-based epidemiology (WBE) to monitor and assess community health through wastewater analysis.

Frederic co-leads the effect-directed analysis working group in the NORMAN network and is the deputy co-leader of Task 4.3 in the European Partnership for the Assessment of Risk from Chemicals (PARC), focusing on innovative methods to monitor contaminants in humans and the environment.

INVITED SPEAKERS

CECILIA GAGLIERO

Univerità degli Studi di Torino

Going greener in analytical extraction for a sustainable characterization of natural products

Cecilia Cagliero (Scopus h-index 28) is Associate Professor in Pharmaceutical Biology at the Department of Drug Science and Technology of the University of Turin (Italy). She obtained her BSc degree in Drug Chemistry and Technology from the University of Turin in 2006 and the PhD degree in Science and High Technology from the same University in 2010.

In 2016, she was a Visiting Professor at the Chemistry Department of Iowa State University (USA). Her research focuses on the development of advanced approaches for the characterization of volatile and non-volatile fractions from plants and natural products.

At the 2016 International Symposium on Capillary Chromatography, she received the Leslie Ettre award (given to a scientist 35 years of age or younger who presented the most interesting original research in the field of capillary gas chromatography) for her presentation on the measurement of acrylamide in coffee powder using gas chromatography/mass spectrometry (GC/MS). In October 2018, she was included in The Analytical Scientist magazine's «Top 40 Under 40 Power List», which aims to identify talented young scientists who are making waves in analytical science.

WEDNESDAY, 23th October 2024

08:30-09:00 **Registration**

09:00-09:30 **Opening Ceremony**

09:30-10:15 **Opening Plenary Lecture**
Chairs:
Ana María García Campaña, University of Granada
Elena González-Peñas, Universidad de Navarra

PL-1: José Bernal del Nozal
University of Valladolid
Determination of contaminants in bee products by using chromatographic techniques (T6)

10:15-11:00 **Oral Communications (OC-Session 1)**
Chairs:
Ana María García Campaña, University of Granada
Elena González-Peñas, Universidad de Navarra

10:15-10:30 Edmondo Messinese (OC-01)
Optimization of an innovative approach for green extraction of bioactive compounds from artichoke and tomato by-products (T6)
University of Parma

10:30-10:45 Jaume C. Morales (OC-02)
Quantitation of over 1,000 pesticide residues in tomato according to SANTE 11312/2021 guideline (T6)
Agilent Technologies

10:45-11:00 Teresa Páramo-Soto (OC-03)
Comprehensive analysis of (poly)phenols in artichoke hearts, stems, bracts and leaves as a base for agro-industrial by product revalorization (T6)
Universidad de Navarra

11:00-12:00 **Poster Session 1 (P1-P15) & Coffee Break & Exhibition**

12:00-13:00 **Oral Communications (OC-Session 2)**

Chairs:
Mario Fernández Martín, Institute of General Organic Chemistry
Jordi Díaz Ferrero, Chemical Institute of Sarriá, Ramon Llull University

12:00-12:15 Julio Lluch (OC-04)
One analyzer, multiple solutions: from MOSH, MOAH, pesticides, and beyond (T6)
LECO Spain&Portugal

12:15-12:30 Eva Gallego (OC-05)
Evaluation of potential sample contamination during volatile organic compounds (VOCs) active air sampling (T4)
Universitat Politècnica de Catalunya

12:30-12:45 Águeda Sánchez-Martín (OC-06)
Adsorption capacity of emerging organic pollutants by activated biocarbons from agricultural waste (T4)
Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC)

12:45-13:00 Núria Fontanals (OC-07)
Wastewater based epidemiology approach to assess pharmaceutical consumption in Spain (T4)
Universitat Rovira i Virgili

13:00-13:45 **Plenary Lecture**

Chairs:
Mario Fernández Martín, Institute of General Organic Chemistry
Jordi Díaz Ferrero, Chemical Institute of Sarriá, Ramon Llull University

PL-2: **Jennifer Kirwan**
Charité University Hospital
The metabolome and the immune system; why good chromatography matters! (T7)

13:45-15:15 **Lunch Break**

15:15-16:15 Oral Young Researchers Communications (OY-Session 1)

Chairs:
Juan Vicente Sancho Llopis, University Jaume I
Francisco Javier Santos Vicente, University of Barcelona

15:15-15:25 Mikaela Rajchman (OY-01)
Chemical characterization of the valorized winery by product *Vitis vinifera* L. cv. Tannat pomace by comprehensive two-dimensional liquid chromatography (LC x LC) (T6)
Institute of Food Science Research - CIAL (CSIC-UAM)

15:25-15:35 Marta Rivas Piña (OY-02)
Extraction of safranal and crocins from *Crocus sativus* using neoteric solvents (T6)
Instituto de Química Orgánica General (IQOR-CSIC)

15:35-15:45 Miriam González-Hernández (OY-03)
Untargeted lipidomics by UHPLC-IMS-QTOF MS for diet intake biomarkers discovery in *Sparus aurata* fish (T6)
Research Institute for Pesticides and Water, University Jaume I

15:45-15:55 Sergi Gregorio-Lozano (OY-04)
Assessment of persistent, mobile and toxic compounds uptake in escarole and tomato plants irrigated with contaminated water in a greenhouse (T6)
Research Institute for Pesticides and Water, University Jaume I

15:55-16:05 Cristian González-Jiménez (OY-05)
Study of whey proteins and caseins behaviour in a nades aqueous biphasic system. Resolving discrepancies in UV and Capillary Electrophoresis results (T3)
Instituto de Química Orgánica General (IQOG- CSIC)

16:05-16:15 Melis Cokdinleyen (OY-06)
Sustainable red seaweed biorefinery: ultrasound, pressurized liquid extraction, and natural deep eutectic solvents integration (T3)
Instituto de Investigación en Ciencias de la Alimentación CIAL (CSIC-UAM)

16:15-17:15 **Poster Session 2 (P16-P29) & Coffee Break & Exhibition**

17:15-17:40 **Poster Flash Discussion Session (PF-Session 1)**

Chairs:
Joan O. Grimalt Obrador, Institute of Environmental Assessment and Water Research
Belén Gómara Moreno, Institute of General Organic Chemistry

17:15-17:20 Araceli Rivera-Pérez (P53)
Identification of key markers revealing the sterilization impact on paprika: Liquid-Chromatography-High-Resolution Mass Spectrometry as a powerful tool (T7)
Universidad de Almería

17:20-17:25 Albert Sales-Alba (P19)
Development of an analytical method of PBDD/Fs in emissions samples (T4)
IQS School of Engineering (URL)

17:25-17:30 Natalia Rodriguez Murillo (P20)
Development of analytical techniques for monitoring PFAS in aquatic environments (T4)
Institut Químic de Sarrià

17:30-17:35 Francisco Soria Prieto (P21)
Method development to the determination of gadolinium contrast agents in peat samples (T4)
Research Institute for Pesticides and Water, University Jaume I

17:35-17:40 Pol Clivillé Cabré (P26)
Chiral determination of amphetamine-type substances in environmental waters by Solid Phase Extraction followed by Capillary Electrophoresis-tandem Mass Spectrometry (T4)
Universitat Rovira i Virgili

17:45-19:30 **SECyTA General Assembly**

20:30 **Welcome Cocktail**

THURSDAY, 24th October 2024

09:00-09:45 **Plenary Lecture**

Chairs:
José A. González Pérez, IRNAS-CSIC
Iziar A. Ludwig Sanz-Orrio, Universidad de Navarra

PL-3: **Frederic Béen**
Vrije Universiteit and KWR Water Research Institute
Novel developments to monitor environmental contaminants and their transformation products in the aquatic environment using high-resolution mass spectrometry and data science (T4)

09:45-11:00 **Oral Communications (OC-Session 3)**

Chairs:
José A. González Pérez, IRNAS-CSIC
Iziar A. Ludwig Sanz-Orrio, Universidad de Navarra

09:45-10:00 Monsalud del Olmo-Iruela (OC-08)
Toxic cyanopeptide monitoring in thermal spring water by capillary electrophoresis tandem mass spectrometry (T4)
University of Granada

10:00-10:15 Pedro Cano (OC-09)
From known to unknown in Mass Spectrometry: an example with PFAS challenge (T1)
Bruker Española S.A.

10:15-10:30 Enriqueta Anticó (OC-10)
New polymeric films and advanced configurations for in-situ extraction of organic pollutants (T3)
Universitat de Girona

10:30-10:45 Michael Soll (OC-11)
"Up in the air, deep on the ground" quantification & identification of microplastics in marine sediments and air by Pyrolysis-GC/MS (T1)
Frontier Laboratories Europe

10:45-11:00 Borja Peris-Camarasa (OC-12)
Fast and eco-friendly analytical method to determine bisphenols, parabens, benzophenone-3 and triclosan in human urine by Ultra-Performance Liquid Chromatography coupled to Mass Spectrometry (T3)
Foundation for the Promotion of Health and Biomedical Research in the Valencian Region, FISABIO – Public Health

11:00-12:00 Poster Session 3 (P30-P43) & Coffee Break & Exhibition

12:00-12:45 Oral Communications (OC-Session 4)
Chairs:
Núria Fontanals Torroja, Universitat Rovira i Virgili
Elena Lizarraga Pérez, Universidad de Navarra

12:00-12:15 Santiago Nicolás Otaiza-González (OC-13)
Antibiotic occurrence and environmental risks assessment in a recirculating aquaculture system (T4)
Institut Català de Recerca de l'Aigua (ICRA-CERCA)

12:15-12:30 Jaap de Zeeuw (OC-14)
Liner selection in Gas Chromatography (T2)
CreaVisions

12:30-12:45 Martí Rosés (OC-15)
Characterization of HPLC sorbents and solvents: a comparison of Tanaka and Abraham methods (T2)
Universitat de Barcelona

12:45-13:45 Round Table on Artificial Intelligence and Chromatography
Chair:
Ángel Irigoyen Barrio, Universidad de Navarra

Panelists:
Ivan Cordón Medrano, DATAI, *Universidad de Navarra*
Ángel Ursúa Sesma, *Tairel Data*
Jaume C. Morales, *Agilent Technologies*
Marta Burrull, *Waters*

13:45-15:15 Lunch Break

15:15-16:00 **Plenary Lecture**

Chairs:
Begoña Jiménez Luque, Institute of General Organic Chemistry
Marta Lores Aguín, University of Santiago de Compostela

PL-4: **Gabriel Vivó-Truyols**
Tecnometrix
Chromatographic big data analysis using Bayesian statistics: finding alternative ways to automation (T7)

16:00-16:25 **Poster Flash Discussion Session (PF-Session 2)**

Chairs:
Begoña Jiménez Luque, Institute of General Organic Chemistry
Marta Lores Aguín, University of Santiago de Compostela

16:00-16:05 Sandra Adámez-Rodríguez (P05)
L-Arginine based chiral ionic liquids for the enantiomeric analysis of amino acids by Electrokenetic Chromatography and Ligand Exchange Capillary Electrophoresis. A comparative study (T2)
Universidad de Alcalá

16:05-16:10 Patricia González Palacios (P31)
Determination of obesogens in biological samples and their relationship to childhood overweight/obesity (T5)
University of Granada

16:10-16:15 Cristian González Jiménez (P32)
Therapeutic monoclonal antibodies analyzed by Capillary Electrophoresis with SDS (T5)
Instituto de Química Orgánica General (IQOG-CSIC)

16:15-16:20 Águeda M. Sánchez-Martín (P36)
Chromatographic analysis of the impact of organic amendments on the composition of soil and fruit in superintensive olive orchards (T6)
Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC)

16:20-16:25 Marta Díez (P46)
Extraction and characterization of bioactive carbohydrates and phenolics from phytoplankton holobionts (T6)
Instituto de Química Orgánica General (IQOG-CSIC)

16:25-17:25 Poster session 4 (P44-P56) & Coffee Break & Exhibition

17:25-18:05 Oral Young Researchers Communications (OY-Session 2)
Chairs:
Núria Fontanals Torroja, Rovira i Virgili University
Jordi Díaz Ferrero, Chemical Institute of Sarriá, Ramon Llull University

17:25-17:35 Irene Romero-Alfano (OY-07)
Optimization of large volume solid phase extraction (LV-SPE) for toxicological assessment of pharmaceuticals in treated waters from Costa Brava (T5)
Institut Químic de Sarrià

17:35-17:45 Aly Castillo (OY-08)
Transit and bioconversion of polyphenols in the digestive and circulatory systems of broilers fed on grape marc-feed (T5)
Universidade de Santiago de Compostela

17:45-17:55 Laura Solé-Domènech (OY-09)
Determination of high production volume chemicals and polycyclic aromatic hydrocarbons in particulate matter by thermal desorption coupled to gas chromatography and mass spectrometry (T4)
Universitat Rovira i Virgili

17:55-18:05 Antonia Merola (OY-10)
Analytical approach for determination of tire rubber additives and their transformation products in silicone bands (T3)
Institute of Environmental Assessment and Water Research (IDAEA-CSIC)

19:45 Conference Dinner

FRIDAY, 25th October 2024

09:30-10:15 **Oral Communications (OC-Session 5)**

Chairs:
Begoña Jiménez Luque, Institute of General Organic Chemistry
Juan Vicente Sancho Llopis, University Jaume I

09:30-09:45 Pere Colomer-Vidal (OC-16)
Long-term evaluation (2003-2022) of PFAS regulation through Scopoli's Shearwaters (*Calonectris diomedea*) from the Western Mediterranean Basin (T4)
Institute of Organic Chemistry (IQOG-SCIC)

09:45-10:00 Xavier Ortíz Almirall (OC-17)
Calibration and deployment of SPATT passive samplers for cyanotoxins analysis in freshwater by isotope dilution-direct water injection LC-MS/MS (T4)
IQS - Universitat Ramon Llull

10:00-10:15 José A. González-Pérez (OC-18)
A strategy to assess soil organic matter quality and explore processes and humification drivers by Direct Analytical Pyrolysis (PY-GC/MS) and Evolved Gas Analysis (EGA-MS) (T4)
IRNAS-CSIC

10:15-11:00 **Plenary Lecture**

Chairs:
Begoña Jiménez Luque, Institute of General Organic Chemistry
Juan Vicente Sancho Llopis, University Jaume I

PL-5: **Cecilia Cagliero**
University of Turin
Going greener in analytical extraction for a sustainable characterization of natural products (T3)

11:00-11:30 **Coffee Break**

11:30-12:45 **Oral Communications (OC-Session 6)**

Chairs:
Ana María García Campaña, University of Granada
Elena González-Peñas, Universidad de Navarra

11:30-11:45 Sara Moreno-Talavera (OC-19)
Systematic evaluation of the metabolome of polar compounds in two sepsis liver models using multiplatform chromatographic techniques coupled to high-resolution mass spectrometry (T7)
Universidad San Pablo-CEU

11:45-12:00 Mercè Garí (OC-20)
Occurrence of tire rubber additives in a natural environment characterized by high wheel traffic (T5)
Institute of Environmental Assessment and Water Research (IDAEA-CSIC)

12:00-12:15 Raúl Alva (OC-21)
Simplified methodology for the analysis of polycyclic aromatic hydrocarbons metabolites in urine. Exposure assessment in children and firefighters (T5)
Institute of Environmental Assessment and Water Research (IDAEA-CSIC)

12:15-12:30 Araceli Rivera-Pérez (OC-22)
Metabolomics based on Liquid-Chromatography-High-Resolution Mass Spectrometry reveals key markers to authenticate the botanical origin of honey (T7)
Universidad de Almería

12:30-12:45 Lucas L. Alonso (OC-23)
Occurrence of wastewater-derived contaminants in two irrigation water systems, and their fate into agricultural soils: spatial analysis and soil risk assessment (T4)
Institut Catalá de Recerca de l'Aigua (ICRA-CERCA)

12:45-13:45 **Closing and Awards Ceremony**

13:45 **Farewell Lunch**

T1. New developments in analytical instrumentation/detection systems

P01-Upgrading an analytical method for the determination of PMT and vPvM substances in groundwater

N. Sáez-Rosique, J. Ma, T. Garrido, M. Exposito, J. Fraile, J. Mas-Pla, J. Radjenovic, M. Gros, S. Rodriguez-Mozaz
Catalan Institute for Water Research (ICRA)

T2. Fundamentals on chromatography and electro-driven separations

P02-Understanding the partition of solutes in columns that mimic biological processes through the Abraham solvation parameter model

Susana Amézqueta, Ana Lucía Valdez, Elisabeth Fuguet, Martí Rosés
Universitat de Barcelona

P03-Chromatographic selectivity in reversed phase and HILIC columns

Xavier Subirats, Ester Lopera, Martí Rosés
Universitat de Barcelona

P04-Biomimetic chromatography: characterization of micellar and microemulsion electrokinetic systems by a fast LFER approach

Rabia Idrees, Xavier Subirats, Susana Amézqueta, Martí Rosés
Universitat de Barcelona

P05-L-Arginine based chiral ionic liquids for the enantiomeric analysis of amino acids by electrokinetic chromatography and ligand exchange capillary electrophoresis. A comparative study

Sandra Adámez-Rodríguez, María Luisa Marina, María Castro-Puyana
Universidad de Alcalá

P06-Global versus individual models to describe retention with isocratic and gradient experiments in RPLC

J.R. Torres-Lapasió, P. Peiró-Vila, M. Blázquez-Mateu, M.C. García-Alvarez-Coque
Universitat de València

P07-Use of individual and global retention models in serial coupling of columns for enhanced selectivity in RPLC

M.C. García-Alvarez-Coque, P. Peiró-Vila, M. Blázquez-Mateu, J.R. Torres-Lapasió
Universitat de València

P08-Combination of sodium dodecylsulfate and 1-hexyl-3-methylimidazolium chloride as mobile phase additives

M.C. García-Alvarez-Coque, C.J. Tereba-Mamani, M.J. Ruiz-Ángel
Universitat de València

T3. Sample preparation methods

P09-Application of the theory of solubility of Hansen to the selection of green solvents for the selective extraction of polychlorinated biphenyls from complex biotic samples

Belén Gómara, Lourdes Ramos
Instituto de Química Orgánica General (IQOG-CSIC)

P10-Natural eutectic solvent screening by Cosmo-RS for the selective bisphenol extraction from soft drinks

Luz Alonso-Dasques, Plácido Galindo-Iranzo, Rosa Lebrón-Aguilar, Belén Gómara, Jesús E. Quintanilla-López
Instituto de Química Física Blas Cabrera (IQF-CSIC)

P11-Efficient removal of natural deep eutectic solvents in extracts: Enhancing purity and bioactivity of bioactive compounds

Victor M. Amador-Luna, Miguel Herrero, Carlos Pajuelo, Elena Ibañez, Lidia Montero
Institute of Food Science Research - CIAL (CSIC-UAM)

P12- Comprehensive analysis of pesticide and fungicide levels in air and urine samples in agricultural areas. Pilot study

Natalia Bravo, Clara Jaén, Barend van Drooge, Joan O. Grimalt
Dept. Environmental Chemistry. Institute of Environmental Assessment and Water Research (IDAEA-CSIC)

P13-Hypercrosslinked sulfonated core shell particles for the selective extraction of pharmaceuticals in environmental samples

Rosa M. Marcé, Alberto Moral, Francesc Borrull, Peter A. G. Cormack, Núria Fontanals
Universitat Rovira i Virgili

P14-Unveiling the role of char incorporated in a poli ε-caprolactone polymer thin film for steroid hormones microextraction

Francesca Merlo, Vincenzo Cerviani, Antonella Profumo, Andrea Speltini, Alba Cabrera, Clàudia Fontàs, Enriqueta Anticó
University of Girona

P15-Computational assessment of monoterpenoids for a sustainable remediation of sulfonamides in water

Ana Ariza-Díez, Plácido Galindo-Iranzo, Rosa Lebrón-Aguilar, Belén Gómara, Jesús E. Quintanilla-López

Instituto de Química Física Blas Cabrera (IQF-CSIC)

T4. Environmental and industrial analysis

P16-Bioacumulation and depuration of three common antibiotics in benthic organisms: sea cucumber, snakelocks anemone and beadlet anemone

Alberto Zafra-Gómez, María del Carmen Gómez-Regalado, Julia Martín, Félix Hidalgo, Juan Luis Santos, Irene Aparicio, Esteban Alonso

University of Granada

P17-Analytical method for the accurate determination of polycyclic aromatic hydrocarbons in black tattoo ink

Juan José Ramos, Sara González, Oscar Fernández, Cristina Grande, Ana Rodríguez, Marta Esteban-López, Ana Cañas-Portilla

Centro Nacional de Sanidad Ambiental, Instituto de Salud Carlos III (ISCIII)

P18-Strategies and routine analysis of PFASs by UHPLC tandem Mass Spectrometry UHPLC-MS/MS during drought periods

Guillem Carrera Ruiz, Aniol Roca Rodríguez, Maria Rosa Boleda Vall-Llobera

Aigües de Barcelona EMGCIA

P19-Development of an Analytical Method of PBDD/Fs in Emissions Samples

Albert Sales-Alba, Xavier Ortiz Almirall, Jordi Díaz-Ferrero

IQS School of Engineering (URL)

P20-Development of analytical techniques for monitoring PFAS in aquatic environments

Natalia Rodriguez Murillo, Marc Marín-García, Núria Agulló Chaler, Jordi Díaz-Ferrero, Cristian Gómez-Canela

Institut Químic de Sarrià, Universitat Ramon Llull

P21-Method development to the determination of gadolinium contrast agents in peat samples

Francisco Soria Prieto, Antoni Francesc Roig i Navarro, Raúl García Cubedo

Research Institute for Pesticides and Water, University Jaume I

P22-Pharmaceutically active compounds (PhACs) in wastewater treatment plants

Silvia Royano, Adrián De la Torre, Irene Navarro, Mª Ángeles Martínez
CIEMAT

P23-Occurrence and transference of pharmaceutically active compounds (PhACs) in sediments and fish from Tagus river basin

Silvia Royano, Adrián De la Torre, Irene Navarro, Mª Ángeles Martínez
CIEMAT

P24-Identification of molecular biomarkers linked to hydrophobicity of crops using High-Resolution Mass Spectrometry

Nicasio T. Jiménez-Morillo, Dalton Everette, Dara Park, Gonzalo Almendros, José A. González-Pérez
IRNAS-CSIC

P25-Bioaccumulation and transformation of plastic additives in hydroponically grown plants: Implications for safe water reuse

M.P. Garcia-Moll, H. Beral, L. Alonso, L.H.M.L.M. Santos, G. Buttiglieri, S. Rodriguez-Mozaz
Catalan Institute for Water Research (ICRA-CERCA)

P26-Chiral determination of amphetamine-type substances in environmental waters by solid phase extraction followed by capillary electrophoresis-tandem mass spectrometry

Pol Clivillé-Cabré, Francesc Borrull, Carme Aguilar, Marta Calull, Núria Fontanals
Universitat Rovira i Virgili

P27-Per- and poly-fluoroalkyl substances (PFAS) in follicular fluid from women undergoing *in vitro* fertilization (IVF) during oocyte retrieval procedure

Pere Colomer-Vidal, Weronika Marynowicz, Anna Ptak, Juan Muñoz-Arnanz, Begoña Jiménez
Instituto de Química Orgánica General (IQOG-CSIC)

P28-Flow-modulation comprehensive two-dimensional gas chromatography for non-target analysis of organic pollutants in environmental samples

Francisco Javier Santos, Pol Chacón, Encarnación Moyano
University of Barcelona

P29-High resolution analysis of biogenic volatile organic compounds (BVOCs) emitted by intact tomato plants using SPE/GC-TOF-MS

Federico Rodrigo, Nicasio T. Jiménez-Morillo, Carmen Rossini, José Mª de la Rosa, José A. González-Pérez
IRNAS-CSIC

T5: Biological, toxicological, and forensic analysis

P30-Gas chromatography–tandem mass spectrometry method for the determination of selected endocrine disruptors in human faeces

Alberto Zafra-Gómez, Inmaculada Moscoso-Ruiz, Samuel Cantarero-Malagón, Ana Rivas
University of Granada

P31-Determination of obesogens in biological samples and their relationship to childhood overweight/obesity

Patricia González-Palacios, Vega Almazán, Cristina Samaniego, Ana Rivas, Alberto Zafra-Gómez
University of Granada

P32-Therapeutic monoclonal antibodies analyzed by capillary electrophoresis with SDS

Rula Rostom-Ajlani, Cristian Gonzalez-Jimenez, Angel Puerta, Mercedes de Frutos
Instituto de Química Orgánica General (IQOG-CSIC)

P33-Risk assessment in analytical method development procedure according to ICH Q14 guideline. Application example

Ángel Irigoyen Barrio, Ana Lobo González, Elena Lizarraga Pérez, Elena González-Peñas
Universidad de Navarra

T6: Food and nutritional analysis

P34-Determination of obesogens in food and their relationship to childhood overweight/obesity

Yolanda Gálvez-Ontiveros, Viviana Ramírez, Lourdes Rodrigo, Ana Rivas, Alberto Zafra-Gómez
University of Granada

P35-Exploring co-exposure of mycotoxins and pesticides through human biomonitoring: effects of conventional and organic diets

Jose A. Gallardo-Ramos, Jesús Marín-Sáez, Vicente Sanchis, Laura Gámiz-Gracia, Ana M. García-Campaña, Maykel Hernández-Mesa, German Cano-Sancho
University of Granada

P36-Chromatographic analysis of the impact of organic amendments on the composition of soil and fruit in superintensive olive orchards

José María De la Rosa, Águeda M. Sánchez-Martín, Jorge Márquez-Moreno, Sara M. Pérez-Dalí, Paloma Campos, Nicasio T. Jiménez-Morillo, Jose Antonio González-Pérez
Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC)

P37-Simultaneous determination of pesticides and mycotoxins in fish feed by UHPLC-HRMS

María Álvarez-Romero, Jesús Marín-Sáez, Laura Gámiz-Gracia, Ana M. García-Campaña, Antonia Garrido Frenich, Maykel Hernández-Mesa
University of Granada

P38-Analytical method implementation for the determination of total amino acids in samples of chickpea flour by High Resolution Liquid Chromatography

María Teresa Murillo-Arbizu, Asier Bazán, José Miguel González, Paloma Virseda, María José Beriain
ISFOOD Research Institute, Public University of Navarra

P39-GC-MSMS 200+ Multi-residue Pesticide Screening Workflow - comparison of conventional 30 m column and LPGC kit

Fernando Rodriguez, Jana Hepner, Joseph Konschnik, and Chris English
Restek Corporation

P40-Liquid chromatography coupled to mass spectrometry as a tool for the design of a novel smoothie formulation with a highly diversified (poly)phenolic profile

Cristina Matías, Cristina del Burgo-Gutiérrez, María-José Sáiz-Abajo, María-Paz De Peña, Iziar A. Ludwig, Concepción Cid
Universidad de Navarra

P41-Optimization of a new SPME GC-MS method for oregano authentication

Sergio Rivas, Ignacio Jimenez-Amezcua, Ainhoa Charles, Ana I. Ruiz, Ana C. Soria
Instituto de Química Orgánica General (IQOG-CSIC)

P42-A novel approach for the green extraction of forskolin from *Coleus forskohlii* root by the use of bio-solvents

Juan J. Matute-Pinos, Ignacio Jimenez-Amezcua, Ana I. Ruiz-Matute, Jesús E. Quintanilla-López
Instituto de Química Orgánica General (IQOG-CSIC)

P43-FIA-MS methodology for the fast detection of adulterants in Damiana (*Turnera diffusa*) extracts

Adal Mena-García, Marina Díez-Municio, Ana I. Ruiz-Matute
Instituto de Química Orgánica General (IQOG-CSIC)

P44-In-Depth analysis of the phytochemical and bioactive profile of 12 species of Adriatic algae by MSPD-UHPLC-QTOF

Aly Castillo, María Celeiro, Diego Iglesias-Gonzalez, Carmen Garcia-Jares, Marta Lores, Kristina Perišić, Krunoslav Aladić, Stela Jokić
Universidade de Santiago de Compostela

P45-Recovery of proteins from grapefruit peels as a source of bioactive peptides: ultrasound assisted extraction, natural deep eutectic solvents and pressurized liquid extraction

Samuel Bernardo-Bermejo, María Luisa Marina, María Castro-Puyana
Universidad de Alcalá

P46-Extraction and characterization of bioactive carbohydrates and phenolics from phytoplankton holobionts

Marta Díez, Juan Pablo de la Roche, Pilar Águila, Ana Cristina Soria, Ana Isabel Ruiz Matute, María Luz Sanz
Instituto de Química Orgánica General (IQOG-CSIC)

P47-Subcritical water extraction combined with enzymatic assisted extraction for protein recovery from lime peels. Characterization of protein hydrolysates

Rosa María Palma-Manrique, María Concepción García, María Castro-Puyana, María Luisa Marina
Universidad de Alcalá

P48-Comparison of chromatographic methods for the analysis of hidroxycitric acid in *Garnicia cambogia* extracts

Inmaculada Luque-Jurado, Adal Mena-García, Angie Julieth Bellaizac-Riascos, Ana Cristina Soria, María Luz Sanz
Instituto de Química Orgánica General (IQOG-CSIC)

P49-Determination of MOSH and MOAH by CGxCG-TOFMS

Julio Lluch, Sebastiano Pantò
LECO SPAIN&PORTUGAL

P50-Profiling black oat avenanthramides and polyphenols

Marta Lores, María Celeiro, Miguel Otero-Otero, Carmen García-Jares, Bernardo Ordás
Universidade de Santiago de Compostela

P51-Phytochemical and antioxidant composition of *Quercus* acorn extracts obtained by Matrix Solid-Phase Dispersion

Diego Gonzalez-Iglesias, Laura Rubio, Francisco Martinez-Vazquez, Aly Castillo, Maria Celeiro, Carmen Garcia-Jares, Marta Lores
Universidade de Santiago de Compostela

P52-Novel Triple Quad approaches for robust and reliable analysis of PFAS in food matrices with Ultimate Sensitivity

Pedro Cano, Miguel Angel Pérez, Juan Gómez, Diego Martin
Bruker Española S.A.

T7: Chemometrics, data processing, and omics techniques

P53-Identification of key markers revealing the sterilization impact on paprika: Liquid-Chromatography-High-Resolution Mass Spectrometry as a powerful tool

Araceli Rivera-Pérez, Manuel Acosta Motos, Antonia Garrido Frenich
Universidad de Almería

P54-Non-Targeted metabolomics for the authentication and differentiation of honey types: A comparative study of commercial and open-source data processing techniques

Juan V. Sancho, Zeinab Tarchichi, Samia Mokh, Tania Portolés
University Jaume I

P55-Enhanced classification of tea varieties using high-performance liquid chromatography and global retention models

J.R. Torres-Lapasió, P. Peiró-Vila, C. Pérez-Gracia, M.C. García-Alvarez-Coque
Universitat de València

P56- Application robustness of the 6495 triple quadrupole LC/MS system for non-stop pesticide analysis in black tea matrix

Jose J. Rivero, Peter Weidner, Patrick Batoon, Behrooz Zekavat, Anabel Fandino
Agilent Technologies

PLENARY LECTURES

PL-1

DETERMINATION OF CONTAMINANTS IN BEE PRODUCTS BY USING CHROMATOGRAPHIC TECHNIQUES

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Bee products, such as honey, beeswax, bee pollen, propolis and royal jelly, have multiple benefits for human health due to their nutritional and medicinal properties (antioxidant, antibacterial, antiviral and anti-inflammatory). Therefore, their consumption has increased in recent years, despite having been valued since ancient times. However, in recent years, several studies have detected contaminants in bee products that are harmful to human health, such as pesticides and plasticizers, which have been much less studied in these matrices. Pesticides can be found in beehives, either due to beekeepers utilizing them to control the damaging effects of the Varroa mite or their potential accumulation in wax, which is directly in contact with other bee products. Moreover, in recent years, there has been a significant increase in plastic production. Nevertheless, despite its usefulness and ubiquity, plastic consumption and disposal are contributing to substantial pollution in the environment. One notable contributor to this pollution is the use of additives, commonly known as plasticizers, like phthalate esters and bisphenols, aimed at enhancing the properties of plastics. However, the use of plasticizers raises health-related concerns, as they can reach numerous matrices, including food consumed by humans as bee products. Consequently, there is a need for efficient, selective, and sensitive methods to determine those contaminants (pesticides and plasticizers) in bee products.

First of all, different analytical methods were optimized involving solvent extraction and modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) followed by a further gas chromatography-mass spectrometry (GC-MS) determination were proposed and validated to determine seven of the most frequently detected pesticides in Spanish bee products such as honey, beeswax, bee pollen, royal jelly and propolis. In some cases, the pesticide levels found in the analyzed samples were higher than those authorized by European current legislation. On the other hand, the analysis of plasticizers required the use of two different chromatographic techniques, depending on the families of compounds studied. Ultra-high-performance liquid chromatography-tandem mass spectrometry was selected for determining fourteen bisphenols in honey and bee pollen. Different sample treatments were evaluated, solid phase extraction, QuEChERS and solvent microextraction. Only two bisphenols were quantified in the honey and pollen samples analyzed, and in all cases, in compliance with current legislation. Meanwhile, GC-MS was selected for determining six phthalate esters, one adipate, and two diphenyl ethers in honey and bee pollen. Different sample treatment options were again tested (dispersive liquid microextraction, QuEChERS and solvent extraction), with the aim to ensure good recoveries, minimize the potential matrix effect, and adhere as closely as possible to the principles of green analytical chemistry. Finally, five of the studied compounds were quantified in some of the analyzed samples, but again, at concentrations lower than the established limits.

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PL-2

DETERMINATION OF CONTAMINANTS IN BEE PRODUCTS BY USING CHROMATOGRAPHIC TECHNIQUES

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Precision medicine promises more tailored prognostic and treatment approaches in the medical world. One tool in the precision medicine toolkit is metabolomics; the global measurement (including characterization and quantification) of small molecules in a biological system. Our lab focuses on how metabolomics can be used to further the aims of precision medicine including diagnostics, prognostics and identifying potential new treatment avenues to explore. In particular, we collaborate on studies which examine the crosstalk between organs, especially the heart, gut and brain and how this is influenced by the microbiome and the immune system. Good metabolomics studies in the medical field rely on careful experimental design, and strong quality management in the analytical lab. This lecture will discuss some of these aspects centring around a case study based on the effects of the microbiome in modulating the immune system and the importance of good chromatography.

PL-3

NOVEL DEVELOPMENTS TO MONITOR ENVIRONMENTAL CONTAMINANTS AND THEIR TRANSFORMATION PRODUCTS IN THE AQUATIC ENVIRONMENT USING HIGH-RESOLUTION MASS SPECTROMETRY AND DATA SCIENCE

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Water resources are increasingly under pressure due to climate change and human activities. The emission of a broad, often unknown range of chemicals presents significant challenges for drinking- and wastewater utilities, environmental laboratories, and regulators. These chemicals include pharmaceuticals, pesticides, biocides, industrial compounds, and personal care products. Adding to the complexity, many of these chemicals undergo transformations in the environment or during treatment, further expanding the chemical space that needs to be monitored. Conventional targeted analytical techniques are insufficient to track the vast array of potential chemicals. High-resolution mass spectrometry (HRMS) has become the method of choice as it allows for the detection of a broader range of chemicals in a single analysis. However, HRMS alone is not enough. Environmental analytical chemists are increasingly combining HRMS with complementary techniques such as orthogonal chromatography, effect-based methods, and advanced data science applications. Notably, the introduction of data visualization and machine learning-based prioritization strategies, which aim to reduce the volume of chemical information and focus on relevant contaminants, is revolutionizing water quality monitoring. The goal of this presentation is to provide an overview of the latest advances in HRMS-based water monitoring strategies, including the integration of complementary techniques and data-driven approaches.

PL-4

CHROMATOGRAPHIC BIG DATA ANALYSIS USING BAYESIAN STATISTICS: FINDING ALTERNATIVE WAYS TO AUTOMATION

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All techniques of data analysis methods applied to chromatographic data, including base-line correction, peak detection, alignment, peak tracking, calibration and/or classification are a routine part of most modern analytical workflows. With the emergence of hyphenation (especially high resolution mass spectrometry) and two-dimensional methods (e.g. GCxGC and LCxLC) we can truly talk about a “Big data” era in analytical chemistry. Analysing these enormous and complex quantities of data becomes a tremendous challenge, especially because of the need of automation.

Automation is always a challenging task. In most of cases, the scientist has to “rely” on the algorithm taking (automated) decisions on both qualitative (e.g. peak identification) or quantitative (e.g. calibration) processes. However, Bayesian statistics really offers a paradigm shift on the automation process. Contrary to classical methods, it is not the algorithm but the scientist the one who takes the decisions, and the role of the algorithm is to calculate the probabilities of the variables of interest. Such probabilities are modified as long as new observations are introduced into the equation. In the end, dealing with (propagated) probabilities allows the scientist to take final (informed) decisions: the role of the algorithm is limited to “inform” the user, instead of taking decisions itself.

This way of thinking has been applied to a broad range of situations in chromatography. One example concerns peak detection in 2D chromatography, in which several configurations may be possible concerning the beginning and the end of a peak, affecting the quantitative results. Another example covers screening techniques, in which the probabilities of a list of compounds being present in the sample are considered, analysed with LC-MS. Another example is a Bayesian deconvolution of chromatographic data, in which the classical multivariate curve resolution (and hence library search, if possible) is applied probabilistically, so the question of parsimony of the model (i.e. how many compounds are present) is solved using Bayesian model averaging. Finally, an application for peak assignment and alignment in LC-MS will be presented, which is tackled from a combinatorial optimization perspective. Surprisingly innovative situations may arise, specially in those cases in which multimodal probability distributions appear, which are in principle counter-intuitive, but, after some reflection, become the best picture of the current knowledge (regarding the scientific question) that the experimental data is able to offer.

All in all, the use of Bayesian statistics to deal with massive data treatment requires a shift in the way of the chromatographer thinks about dealing with data. Basically, we are proposing to work with probability distributions (opposed to fixed parameters), and update them as long as more information/data is taken into account. This is opposed to deliver the final answer to the user.

PL-5

GOING GREENER IN ANALYTICAL EXTRACTION FOR A SUSTAINABLE CHARACTERIZATION OF NATURAL PRODUCTS

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The analysis of natural products and foodstuffs must cover a wide range of topics, from metabolomics studies to quality and safety controls. In all cases, sample preparation plays a fundamental role, as downstream analyses only detect the previously extracted metabolites. Therefore, the choice of the most appropriate extraction approach is of utmost importance and the most critical parameter to be considered, also taking into account the complexity of plant and food samples.

Most studies and official methods for these matrices still use traditional extraction techniques, which have a significant impact on the environment. However, the development of new and more environmentally friendly alternatives that are more in line with the principles of Green Analytical Chemistry has been increasing in recent years. Strategies include the use of miniaturized techniques and new classes of more environmentally friendly extraction phases [1]. However, it is also important to remember that accurate and reliable measurements are required, especially for industrial quality control laboratories that have to deal with a variety of norms and quality standards to ensure safe products for the population, and that practical considerations such as productivity, cost and simplicity of methods should not be neglected [2].

This contribution explores the possibility of improving the environmental footprint of sample preparation while maintaining adequate analytical performance and laboratory productivity. A series of case studies dealing with the extraction of chemically diverse, specialized metabolites from food and natural products will be presented. The attention will be focused in particular on the opportunities offered by the use of renewable and tailorable materials in combination with microextraction techniques and technologies that enable to improve extraction kinetics, such as microwave-assisted extraction. In addition, the presented methods will be evaluated in terms of their overall performance (including the chromatographic separation step) using appropriate metric tools [3-5]. The aim is to move towards “sustainable" analytical methods, where the improvement in terms of environmental impact is assessed together with productivity and analytical performance, which should ensure high quality health products for all.

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ORAL COMMUNICATIONS

OC-01

OPTIMIZATION OF AN INNOVATIVE APPROACH FOR GREEN EXTRACTION OF BIOACTIVE COMPOUNDS FROM ARTICHOKE AND TOMATO BY-PRODUCTS

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Nowadays, agri-food industries generate a considerable volume of by-products generally wasted and under-valorized, but still rich in valuable bioactive compounds with significative nutritional and biotechnological relevance. In a context of a sustainable industrial scalability, a green innovative approach was used for the valorization of artichoke by-products (ABP) and tomato by-products (TBP) generated from industrial processing. Pressurized Liquid Extraction (PLE) was employed and a multilevel factorial design using response surface methodology (RSM) was developed to evaluate the optimal conditions to maximize bioactive compounds recovery and antioxidant capacity. The global yield, total phenolic content, total flavonoid content and antioxidant activity (via ORAC and DPPH assays) were selected as response variables to study the effects of temperature (50-180°C) and solvent composition (mixtures of ethanol/ethyl acetate for ABP, cyclopentyl ether:ethyl acetate for TBP). Software predictions of the optimal extracts were experimentally confirmed: 180°C was the effective temperature able to enhance the response variables; regarding the solvent mixture composition, etanol:ethyl acetate (10:90, v/v) was selected as the best condition for ABP extract, and pure CPME for ABP.

Further investigations were performed to evaluate the *in-vitro* neuroprotective potential of each optimal extract through inhibition assays of acetylcholinesterase (AChE), butyrylcholinesterase (BChE) and lipoxigenase (LOX) enzymes. ABP optimal extract provided better inhibitory ability in terms of IC_{50} than TBP for all these variables.

The analytical characterization and tentative identification of bioactive compounds of the optimal extracts was carried out through UHPLC-q-TOF-MS/MS analysis. Besides, Parallel Artificial Permeability Assays – Blood Brain Barrier (PAMPA-BBB) test was performed to determine the nature of those compounds that could diffuse through the brain membrane. Finally, molecular docking simulations were employed to investigate potential interactions between the most abundant compounds occurring in each PLE optimal extract and the AChE, BChE, LOX catalytic sites able to exert inhibitory effects.

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OC-02

QUANTITATION OF OVER 1,000 PESTICIDE RESIDUES IN TOMATO ACCORDING TO SANTE 11312/2021 GUIDELINE

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A comprehensive multiresidue workflow was developed and validated for the simultaneous quantitation of over 1,000 pesticide residues in tomato to accelerate and simplify routine laboratory food testing. The workflow analyzes a wide range of pesticide residues simultaneously in 20 minutes and uses a single sample preparation method for both LC/MS/MS and GC/MS/MS analyses, leading to increased turnaround time, simplified analysis, and lower laboratory costs.

The workflow includes sample preparation, chromatographic separation, mass spectrometric (MS) detection, data analysis, and data interpretation using Agilent LC/MS/MS and GC/MS/MS systems. For sample preparation, the Agilent QuEChERS extraction kit was used without further cleanup. Compound transitions and associated optimized parameters were developed based on the Agilent pesticide MRM databases for both LC/MS and GC/MS workflows.

Workflow performance was evaluated and verified according to the SANTE 11312/2021 guideline based on instrument limit of detection (LOD), calibration curve linearity, recovery, and precision using matrix-matched calibration standards from 0.5 to 100 µg/L. Over 98% of analytes demonstrated linearity with $R^2 \geq 0.99$. Method precision was assessed using recovery repeatability (RSDr). At the 10 µg/kg level, RSDr values of 98% of compounds were within the limit of 20%. The mean recoveries of the six technical replicates were within the limits of 40 to 120% for 98% of target analytes.

OC-03

COMPREHENSIVE ANALYSIS OF (POLY)PHENOLS IN ARTICHOKE HEARTS, STEMS, BRACTS, AND LEAVES AS A BASE FOR AGRO-INDUSTRIAL BY PRODUCT REVALORIZATION

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Artichoke is a vegetable rich in Hydroxycinnamic Acids (HCAs) [1]. These compounds have been reported to benefit the management and prevention of chronic diseases, such as Type 2 Diabetes (T2D) [2, 3]. Artichoke's stems, bracts, and leaves are mostly discarded postharvest as by-products, although they may be a rich source of bioactive compounds.

This research aimed to screen the four main parts of the artichoke plant (hearts, stems, bracts, leaves) for their (poly)phenolic profile, as a preliminary step to explore the potential reuse of the by-products in T2D prevention supplements.

(Poly)phenolic profile and concentration of hearts, stems, bracts and leaves from 6 artichokes (Cynara scolymus L. cv. Blanca de Tudela) were assessed by high-performance liquid chromatography coupled to a triple quadrupole linear ion trap mass spectrometer (LC-ESI-MS/MS), based on the method described by Dominguez-Fernandez M. et al. 2021 [1]

Twenty-two compounds were identified and quantified in the different artichoke parts. All by-products exhibited high (poly)phenol concentrations. Hearts, stems, and bracts had a similar profile, detecting 17, 12, and 15 compounds respectively, with acyl-quinic acids (mainly 5-CQA, 1,5-diCQA, 3,5-diCQA) constituting over 98% of total concentrations. Fifteen (poly)phenols were detected in leaves, with flavonoids contributing over 50% of total concentration, while 1,5-diCQA and 3,5-diCQA were hardly present. Considerable variations in total and individual (poly)phenols concentrations were observed among the 6 artichokes, especially in leaves.

The high (poly)phenol concentrations found in artichoke by-products suggest their potential use as supplements for chronic disease prevention. This study also provided an in-depth qualitative and quantitative characterization of their (poly)phenolic profile, identifying discriminating compounds between different artichoke parts.

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OC-04

ONE ANALYZER, MULTIPLE SOLUTIONS: FROM MOSH, MOAH, PESTICIDES, AND BEYOND

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Comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC×GC-TOFMS) is nowadays considered a robust analytical technique for the detection and quantification of various target and non-target compounds in food matrices.

This technique has already proven to be highly effective for the qualitative analysis of Mineral Oil Hydrocarbons (MOH), revealing markers of contamination (e.g., hopanes, dibenzothiophenes, diisopropylnaphthalenes, POSH, PAO) as well as natural interferences (e.g., terpenoids).Recently, LECO also introduced a more advanced solution, including a GC×GC-FID channel within the same hardware setup, enhancing the accuracy of quantification for these fractions while using GC×GC-MS data to support quantitative results.

Due to the intrinsic characteristics of TOFMS, such as the acquisition of full-mass range data with superior sensitivity, similar or slightly adapted methods can also be used to detect and quantify other compound classes, both as targets but also as unknowns, with simultaneous high quality non-target data collection. This adaptability addresses additional complex analytical challenges. For instance, we have applied nearly the same method to detect and quantify pesticide residues in food commodities and furans/methyl furans in coffee and coffee-substitute samples, ensuring compliance with regulatory standards, whilst obtaining significant insights into the presence of other residues and sample characterising analytes such as aroma active species.

Examples of the combined analytical methods will be presented, highlighting the synergistic effect of using one technology to address multiple analytical questions.

OC-05

EVALUATION OF POTENTIAL SAMPLE CONTAMINATION DURING VOLATILE ORGANIC COMPOUNDS (VOCs) ACTIVE AIR SAMPLING

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The main objective of volatile organic compounds (VOCs) air sampling is to collect target compounds to evaluate their concentrations in emission sources and determine air quality in ambient air both indoors and outdoors. Monitoring specific industrial processes or odorous/pollution episodic events requires from precise samplings during definite periods of time, being the use of active sampling recommended [1-2]. Accordingly, the sampling strategy has to fulfill several aspects: be representative, simple to use, no degradation and losses must occur during sampling, storage and analysis, and finally, no contamination must result during sampling [3-5]. Several experiments were carried out for the evaluation of possible sampling contamination in self-designed active samplers that use sorbent tubes for VOCs collection. These sampling devices have been developed at our laboratory and are composed of two valves at each extent of the sampling tube, allowing the air pass through the tube during sampling and preventing it when not sampling. As episodic pollution events may last only a few minutes, the collection of more than a single episode in a sample may be needed for proper analysis. Hence, sorbent tubes may have to be placed during several days on the sampling device [2]. Three types of valves were evaluated for possible VOC contamination through diffusion: two types of non-return valves and a solenoid valve. Sorbent tubes were connected to the different valves during 15 days (9 tubes for non-return valves #1, 5 tubes for non-return valves #2 and 10 tubes for solenoid valves) and placed in a neutral office environment. Additionally, the same amount of blank tubes was placed near the tubes connected to the valves, in order to determine possible contamination of the tubes coming from background. Results showed that non-return valves #1 and #2 emitted non-negligible amounts of aromatic hydrocarbons, ethers and siloxanes, showing values of 199±36 ng and 154±37 ng, 55±14 ng and 35±14 ng, and 169±60 ng and 554±320 ng, per tube respectively. On the other hand, solenoid valves were the ones showing less contaminated tubes, as VOCs profiles observed in the sampling tubes were very similar to the ones from the blank tubes, which showed mainly a contribution of the most volatile compounds present in the environment where the experiments took place: acetaldehyde, ethanol and acetone, with contributions of 80±57 ng, 24±8 ng and 73±26 ng, per tube respectively.

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OC-06

ADSORPTION CAPACITY OF EMERGING ORGANIC POLLUTANTS BY ACTIVATED BIOCARBONS FROM AGRICULTURAL WASTE

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The pressing environmental issues facing our planet today demand the development of studies aimed at addressing these challenges. Key concerns include the scarcity of quality drinking water and the efficient management of agricultural waste. Recent advancements in chromatographic techniques, characterized by their low detection limits [1], have facilitated the detection of emerging organic pollutants (EOPs) such as pesticides, antibiotics, and other pharmaceuticals in drinking water. This study evaluates the potential of various abundant agricultural wastes, including rice husks and almond shells, as raw materials for water filters following a comprehensive physicochemical characterization. These wastes exhibited significant carbon content, 38.4% in rice husks and 45.4% in almond shells, suggesting their suitability as precursors for producing activated carbons [1]. The production of activated carbons involved different activation techniques, including chemical activation with potassium hydroxide (KOH) and physical activation using steam.

The efficacy of these activated carbons as filtration media was tested on drugs dissolved in water, aiming to assess their utility in water purification. These analyses involved adsorption tests followed by quantifying the percentage of EOPs adsorbed using high-performance liquid chromatography (HPLC) [2]. Activated carbons from rice husks exhibited high adsorption rates, achieving complete removal (100%) of some contaminants, whereas those from almond shells yielded less favorable results.

In conclusion, this study demonstrates that activated carbons derived from rice husks have the potential to serve as effective filters for drug removal in water treatment processes, while those from almond shells may not be optimal for such applications.

Acknowledgements

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OC-07

WASTEWATER BASED EPIDEMIOLOGY APPROACH TO ASSESS PHARMACEUTICAL CONSUMPTION IN SPAIN

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Wastewater-based epidemiology (WBE) is a consolidated approach to assess the consumption of biomarkers excreted by the population through the analysis of influent wastewater (IWW) samples. Concentrations of these biomarkers in IWW are converted to population-normalized daily loads (PNDL, in mg/day 1000/inhabitants), which are then multiplied by a specific correction factor to provide measured consumption [1]. Recently, besides WBE studies on alcohol, tobacco, caffeine, illicit drugs, and new psychoactive substances [1,2], WBE application has also been extended to a number of studies addressing pharmaceutical consumption and correlating this estimated consumption with data on pharmaceutical prescription [1-3]. However, some bias of uncertainty can be found, since pharmaceutical prescription figures may not picture all pharmaceutical consumption.

This study developed an analytical method based on solid-phase extraction followed by liquid chromatography with tandem mass spectrometry to monitor a group of 17 pharmaceuticals, including the most representative ones of the main therapeutic families in IWW samples. Samples were collected over a week campaign in four different wastewater treatment plants (WWTPs) across Spain. The method provided successful recoveries (35%-140%) and matrix effects (-64 to +47), and method quantification limits below 300 ng/L in such complex samples.

Data on pharmaceutical occurrence were transformed into measured pharmaceutical consumption (MC) and compared to the data on dispensed pharmaceuticals in pharmacies from the region where the WWTP catchment area is located, to end with dispensed consumption (DC) data. The level of correlation among MC/DC is higher than those reported so far, with ratios within 0.8 to 1.2 order for 11 out of the 17 studied pharmaceuticals.

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OC-08

TOXIC CYANOPEPTIDE MONITORING IN THERMAL SPRING WATER BY CAPILLARY ELECTROPHORESIS TANDEM MASS SPECTROMETRY

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Cyanobacteria are an ancient group of prokaryotes capable of oxygenic photosynthesis. They are a prolific source of natural products and produce a vast array of compounds, including many notorious toxins. Recently thermal crises in hot springs have been associated with the presence of cyanopeptides [1]. Similarities have been detected with the symptoms produced by acute cyanotoxin poisoning.

In line with the trend in green analytical chemistry, the aim of this work is to develop a fast, easy and reliable method to monitor the presence of cyanopeptides in geothermal springs located in Granada (Spain) with a broad range of thermal characteristics (temperature and conductivity particularly). Two sampling periods were programmed: in June and September. The biomass was also characterized to reveal the possible presence of cyanobacterias. The analytical method based on capillary zone electrophoresis coupled to tandem mass spectrometry (CZE-MS/MS) was developed to quantify simultaneously 15 cyanopeptides. A basic 50 mM ammonium acetate buffer at pH 10.3 was selected as background electrolyte since satisfactory peak efficiency and resolution were achieved. A remarkably low analysis time of just 7 minutes was required to determine the 15 compounds. Satisfactory results were obtained using Field Amplified Sample Stacking (FASS) as on-line preconcentration strategy by simply using a mixture of H_2O:MeOH (90:10, *v/v*) as injection solvent. Parameters affecting electrospray conditions were carefully studied, including sheath liquid flow rate (10 µL/min) and composition (MeOH:H2O:FA, 30:69,7:0.3 v/v), nebulizer pressure (12 psi), dry gas flow rate and temperature (11 L/min, 150 °C), sheath gas flow rate and temperature (5 L/min, 195 °C) and ESI and nozzle voltages (2000 V for both). A triple quadrupole operating in multiple reaction monitoring (MRM) was employed with positive electrospray ionization. This operation mode provided the highest sensitivity when certain parameters such as the dwell time and particularly the collision energy were properly selected. For sample treatment, a salting-out assisted liquid-liquid extraction (SALLE) protocol was optimized for thermal water. Acetonitrile was used as extraction solvent and $MgSO_4$ as auxiliary salting-out agent. The proposed method shows a high sensitivity, selectivity and efficiency.

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OC-09

FROM KNOWN TO UNKNOWN IN MASS SPECTROMETRY: AN EXAMPLE WITH PFAS CHALLENGE

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We will present some of the analytical challenges related with PFAS determination, in different matrices and scenarios. As you all know PFAS determination due to their huge family of compounds and their presence in virtually everywhere, it is one of the most interesting and demanding analytical challenges nowadays.

From a known list of compounds, as it is required by law in food or water samples, we will show the workflow optimized with the best technology designed for this kind of job driven by the new LCMS DART TQ+ Platform for ultimate sensitivity and robustness.

The unknown, is a complementary vision for family identification and non-target analysis, using the most advanced high resolution mass spectrometry systems with trapped ion mobility devices or not, showing analytical workflows able to solve this challenging analytical puzzle.

OC-10

NEW POLYMERIC FILMS AND ADVANCED CONFIGURATIONS FOR IN-SITU EXTRACTION OF ORGANIC POLLUTANTS

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The constantly increasing amount of pollutants in the aquatic environment is a shameful consequence of human activity. Pesticides, extensively used in agriculture during many years, are still present in surface waters resulting in a threat for living organism and a deterioration of both water quality and the ecological status of the water body. Therefore, the monitoring of trace levels of organic pollutants is of paramount importance. The conventional methods for water monitoring (grab sampling) require the collection of a large volume of water samples. Furthermore, these methods cannot completely account for alterations due to uncontrolled changes in flow, precipitation or episodic inputs. For that, passive samplers based on different sorbents have been developed. Although some of them are commercially available, they present serious limitations due to the wide range of organic pollutants bearing different chemical behavior. For this reason, the preparation of new materials together with different sampler configurations is of great interest.

Polymeric films can be used as a material for the extraction of organic compounds, as we have demonstrated in previous publications [1,2]. In this work, polymeric films modified with deep eutectic solvent (DES) and multiwalled carbon nanotubes (MWCNT) were synthesized and tested for the passive sampling of the pesticide chlorpyrifos. The modified films were prepared by the solving casting method, with the polymer cellulose triacetate (CTA) and as a deep eutectic solvent, the mixture dodecanoic acid:lidocaine (2:1) [3]. Different film compositions and configurations for the passive sampler were essayed. In particular, the compositions tested were 70%CTA:30%DES, 90%CTA:10%DES, 90%CTA:10%MWCNT, and 80%CTA:10%MWCNT:10%DES. After extraction, the ultrasound-assisted elution was performed with ethyl acetate or ethanol, followed by GC-MS analysis. For *in situ* application, the film 70%CTA:30%DES was placed either in a Teflon holder with polyvinylidene fluoride or polyethersulfone filters, or in a dosimeter where the film is sandwiched between two methacrylate disks, fixed with screws, with a central window. Differences in stability and performance for deployment times up to one week were found for the different film composition and configuration.

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OC-11

“UP IN THE AIR, DEEP ON THE GROUND” QUANTIFICATION & IDENTIFICATION OF MICROPLASTICS IN MARINE SEDIMENTS AND AIR BY PYROLYSIS-GC/MS

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Environmental pollution by plastics has become one of the most serious environmental issues. Microplastics may affect marine life by accumulating in the food chain and have a possible impact on human health. Therefore, analysis of microplastics in the environment is of interest. In this study, a vertical furnace pyrolyzer coupled to GC/MS (Py-GC/MS) was applied to microplastics analysis, since it provides high-sensitivity analysis and quantitative data even when the sample is a mixture of multiple polymers. The analytical workflow and instrumental setup are described. A dedicated software using a new search algorithm[1] and mass spectral libraries was applied to identify and quantify micro plastics. Software features and step-by-step workflow is demonstrated. The libraries contain 11 and 12 abundant plastic types. For easy weighing of µg scale of polymers and to consider polymer-polymer side reactions, a Micro Plastic Calibration Standard Mixture [2] was used. A dedicated micro plastic GC column setup, containing a Precolumn and analytical separation column is improving chromatographic resolution. A newly developed multifunctional sampler (MFS) for splitless pyrolysis[3] without secondary reactions is used to increase S/N ratio, thus improving limit of quantification of trace level micro/nano plastics. In the first study, offshore and coastal sediment samples have been analysed. After data analysis using the micro plastic search software, various plastic types could be detected and quantified. In the second study, we investigated the analysis of indoor airborne microplastics by Py-GC/MS [4]. Indoor air was passively sampled using quartz fiber filters. Sample preparation was limited and consisted only of cryo-milling the quartz filters used for sampling to ensure homogeneity. The results demonstrate that MFS enabled Splitless Py-GC/MS can be used to identify and quantify microplastics at the nanogram level, allowing researchers to rapidly ascertain the magnitude of the microplastic threat in environmental air.

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OC-12

FAST AND ECO-FRIENDLY ANALYTICAL METHOD TO DETERMINE BISPHENOLS, PARABENS, BENZOPHENONE-3 AND TRICLOSAN IN HUMAN URINE BY ULTRA-PERFORMANCE LIQUID CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY

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Bisphenols, parabens, benzophenone-3 and triclosan are synthetic chemicals commonly used in various products such as cosmetics, pharmaceuticals and food items, leading to human exposure through ingestion, dermal contact and inhalation. Once entering the body, they are rapidly absorbed, metabolised, and excreted in urine due to their short half-lives. Recognized as potential endocrine-disrupting chemicals (EDCs), they have raised concerns among researchers and regulatory bodies. In response to the concerns regarding environmental harm and risks, innovative analytical strategies are required based on the new criteria focused on the twelve principles of Green Analytical Chemistry. Therefore, a new methodology for the environmentally friendly, fast, efficient and simultaneous determination of nine potential EDCs in human urine, including three bisphenols (A, F and S), four parabens (methyl, ethyl, propyl and butyl parabens), benzophenone-3 and triclosan, has been developed and validated. It is based on a dilute-and-shoot method and ultra-performance liquid chromatography coupled to tandem mass spectrometry analysis. The relative recoveries ranged from 80 % to 120 % with a precision lower than 20 % for all analytes. The concentration ranges obtained encompass the published levels of the compounds in urine and the limits of quantification were between 0.2 and 0.5 ng·mL^{-1}. The proposed method is the most environmentally friendly and practical so far and it was successfully applied for the determination of these compounds in several human urine samples from adults residing in the Valencian Region (Spain), and initial findings suggest that methyl paraben, benzophenone-3 and ethyl paraben were the predominant compounds.

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OC-13

ANTIBIOTIC OCCURRENCE AND ENVIRONMENTAL RISKS ASSESSMENT IN A RECIRCULATING AQUACULTURE SYSTEM

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Antibiotics from human and veterinary sources pose risks to non-target species, contribute to antibiotic resistance, and contaminate various water bodies, potentially disrupting ecosystems and impacting human health. This study evaluates the presence of antibiotics in a Recirculating Aquaculture System (RAS) and its surroundings.

Research was conducted at a commercial RAS facility in Orbetello, Tuscany, Italy. Sampling in July 2023 included a negative control, two fish cages, and inlet/outlet recirculated water points. Water samples were pre-concentrated using Oasis HLB cartridges, and sediments processed by freeze-drying and sieving following a QUEChERS methodology[2]. Fish fillets were freeze-dried and extracted with zirconium beads[3]. Antibiotics were analyzed using LC-MS/MS with matrix-matched calibration[4], and fish samples for antibiotic transformation products (TPs) using UPLC-HRMS. Environmental risk was assessed via Risk Quotients, comparing Maximum Environmental Concentrations to Predicted No-Effect Concentrations, while the Human Health Risk Assessment evaluated Hazard Quotients, relating Estimated Daily Intake to Acceptable Daily Intake.

Sulfonamides, macrolides, and nitroimidazoles were detected in seawater (46 ng/L erythromycin), while sediments showed erythromycin (1 ng/g, dw). Farmed fish contained ofloxacin, azithromycin, norfloxacin, and enrofloxacin, likely from anthropogenic sources. Azithromycin posed moderate risks in seawater; erythromycin showed high risks (RQ >1). Human Health Risk Assessment found no anticipated risk from antibiotic accumulation in fish. Additionally, we identified a significant number of antibiotic TPs in fish at high confidence levels.

Detection of antibiotics in fish, water, and sediments highlights external contamination sources. Moderate to high risks associated with certain antibiotics in seawater emphasize threats to marine ecosystems. Continuous monitoring and mitigation are crucial for safeguarding marine environments and aquaculture integrity.

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OC-14

LINER SELECTION IN GAS CHROMATOGRAPHY

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In GC one can choose from many different liners. There are however a few basic selection criteria that can help you to choose the best liner for your application. Liner selection depends first on injection technique and whether the sample is a liquid or a gas. Additionally, some sample matrices and/or components show challenges to evaporate and transfer, which needs special attention for selecting the optimal liner. As the chromatographic process starts in the liner it is very important that liners are robust and highly inert. Special deactivations and test protocols have been developed to develop such liners. In this presentation we will provide guidelines for liner selection and how liner lifetime can be maximized.

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OC-15

CHARACTERIZATION OF HPLC SORBENTS AND SOLVENTS: A COMPARISON OF TANAKA AND ABRAHAM METHODS

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Selection of the best HPLC stationary-mobile phases combination for a particular separation problem requires a good characterization of the solute-solvent interactions in the chromatographic system. The information provided in this characterization should help in the selection of HPLC systems with the appropriate selectivity. Numerous studies on the characterization of the interactions and selectivity of HPLC phases have been published. Among them, Tanaka's and Abraham's methods have been by far the most successful.

In 1989, Tanaka and co-workers [1] proposed a quick and straightforward methodology to characterize C18 stationary phases combined with specific mobile phase compositions. Similar based tests have been proposed by many other authors [2]. The method is mainly based in the measurement of the selectivity ($\alpha = k_1/k_2$) of pairs of solute indicators (1 and 2 subscripts). For neutral selectivities, pentylbenzene/butylbenzene pair measures hydrophobicity, triphenylene/*o*-terphenyl pair steric selectivity, and caffeine/phenol pair hydrogen bond capacity.

A few years later, the general LFER method of Abraham [3], which characterizes the solute-solvent interactions in many physicochemical and biological processes, was extended to liquid chromatography [4]. In this method, also called solvation parameter model, the solute-(stationary vs. mobile phases) interactions are determined from the retentions ($\log k$) of a set of appropriate solutes in terms of stationary-mobile phase differences in cavity formation, hydrogen bond acidity and basicity, and dipolarity/polarizability. The method requires the multiple linear regression of the retention against the well-known descriptors of a wide set of varied solutes. Recently, we have developed a much faster characterization method [5] which uses simple pairs of solutes like in Tanaka's method.

In this presentation, we shall discuss and compare the specific information provided by both methods, showing their similarities and differences. The main purpose is establishing some guidelines for the selection of the most appropriate stationary-mobile phase system for the separation problem at hand.

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OC-16

LONG-TERM EVALUATION (2003-2022) OF PFAS REGULATION THROUGH SCOPOLI'S SHEARWATERS (*CALONECTRIS DIOMEDEA*) FROM THE WESTERN MEDITERRANEAN BASIN

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Per- and polyfluoroalkyl substances (PFAS) are persistent synthetic chemicals widely used for their surfactant properties and stability [1]. Despite regulatory actions since the early 2000s, PFAS continue to accumulate in wildlife globally, posing environmental and health risks [2]. Seabirds, such as Scopoli's shearwaters, serve as important indicators of PFAS contamination in marine ecosystems [3]. This study focuses on PFAS levels in Scopoli's shearwater livers in the Mediterranean Basin from 2003 to 2022, assessing trends within international regulatory frameworks. PFAS concentrations in Scopoli's shearwaters ranged from 10.5 to 365 ng/g wet weight over four periods (2003-2008, 2009-2014, 2015-2018, and 2019-2022), with PFOS being predominant most of the time, followed by PFTrDA, PFUnDA, PFTeDA, and PFDoDA. Concentrations decreased significantly, with a reduction of approximately 77% by 2022 compared to 2003-2008 [4]. Specific compounds like PFHxS, n-PFOS, Br-PFOS, PFDS, and FOSA decreased notably from 2003-2014. Specific compounds like PFHxS, n-PFOS, Br-PFOS, PFDS, and FOSA decreased notably from 2003-2014 due to the first ban of PFOS in SC 2009. A notable decline in long-chain PFCAs was observed primarily after 2015, corresponding to the implementation of the PFOA Stewardship Program [5, 6]. A PCA highlighted shifts in PFAS bioaccumulation trends over time, likely reflecting the influence of regulatory measures [5]. The study indicates significant temporal trends in PFAS contamination in Scopoli's shearwater livers over two decades, with notable declines in PFOS levels post-2009 regulations [4]. However, non-significant decreases were observed from 2015 to 2018, likely due to changes in historic precursor usage [5]. Regulatory actions have played a crucial role, with increases noted in PFHxS and FOSA post-2009 regulations [4]. Long-chain PFCAs like PFUnDA and PFTrDA decreased in later periods (2015-2022) due to international regulatory actions and production shifts [5]. These findings underscore the effectiveness of global regulations in reducing PFAS levels over time, despite challenges posed by precursor emissions and atmospheric transport. Continued monitoring is essential to assess ecological impacts and track emerging contaminants in marine bird species such as Scopoli's shearwaters.

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OC-17

CALIBRATION AND DEPLOYMENT OF SPATT PASSIVE SAMPLERS FOR CYANOTOXINS ANALYSIS IN FRESHWATER BY ISOTOPE DILUTION-DIRECT WATER INJECTION LC-MS/MS

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Due to the increasing global temperatures caused by climate change and the intensive use of fertilizers in the agricultural industry, the presence of cyanobacteria in freshwater is becoming more common worldwide. The occurrence of these Harmful Algal Blooms (HABs) can be particularly detrimental in the drought conditions currently experienced in Catalunya, where reservoirs levels are below 25%, contributing to an increase in their nutrient concentration (eutrophication) and water temperature. These cyanobacterial HABs can produce different cyanotoxin families like microcystins or anatoxins -among many others-, which can be lethal to aquatic organisms [1] and affect the drinking water supply [2].

One of the main challenges in cyanotoxin analysis is sampling uncertainty, due to the heterogeneous nature of algal blooms, forming colonies of different cell concentration in both water surface and water column, and heavily impacted by wind, sun and water currents. To address this issue, an alternative to traditional water grab sampling is the use of passive samplers.

Passive samplers are commonly based on solid adsorbents that can capture contaminants in the air or water compartments over longer periods of time, lowering the method detection limits by a preconcentration effect, and averaging the contaminant levels over the deployment time. Although passive samplers based on SPATT (Solid Phase Adsorption Toxin Tracking) adsorbents have been used in the past for cyanotoxins (with focus on anatoxin-a)[3], they have never been calibrated in laboratory conditions to determine their sampling rates (Rs), preventing the conversion of the concentration of the toxin in the adsorbent (ng toxin per g of adsorbent) to the water phase (ng toxin per liter of water)[4].

In the present study, SPATT passive samplers have been calibrated and Rs for anatoxin-a and microcystin-LR, -RR, -YR, -LA have been experimentally determined. These values have been employed to estimate the concentration of cyanotoxins in several reservoirs from Catalunya. Microcystin and anatoxin-a analysis has been carried out by isotope dilution-direct water injection LC-MS/MS using 15N and deuterium labelled internal standards, for an improved method accuracy, robustness and throughput.

OC-18

A STRATEGY TO ASSESS SOIL ORGANIC MATTER QUALITY AND EXPLORE PROCESSES AND HUMIFICATION DRIVERS BY DIRECT ANALYTICAL PYROLYSIS (PY-GC/MS) AND EVOLVED GAS ANALYSIS (EGA-MS)

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Soil organic matter (SOM) is an important factor in carbon sequestration that helps mitigate global change. Human activities such as land-use changes, agriculture, and forestry management can affect SOM dynamics. There is a need to assess agricultural measures to increase root carbon inputs to the top and subsoil i.e. practices like no-till agriculture or reforestation can lead to the accumulation of organic matter (OM) [1]. However, an increase of SOM content is not relevant in terms of C sequestration in soils; the SOM transformations resulting from its origin or evolution (humification) in the soil, confer varying degrees of resistance to biodegradation, which is critical to enhancing an effective soil carbon sequestration [2]. In this work, we present a direct strategy that can be used to characterize SOM chemical structure and to evaluate the primary chemical processes that occur during its evolution in the soil. The proposed plan combines analytical pyrolysis (Py-GC/MS) with a graphical statistical approach based on Van Krevelen diagrams [3] and Evolved Gas Analysis (EGA-MS). The Van Krevelen plots have the advantage of displaying the SOM chemical components released during the pyrolysis in different regions of the H/C vs. O/C plane, which facilitates comparisons between samples and the possibility of inferring the main biogeochemical processes that may be involved in SOM stabilization i.e. dehydration, aromatization, dealkylation, decarboxylation, etc. [4]. On the other hand, the EGA provides valuable complementary information about the general SOM chemical composition, a mass spectrum of the evolved gasses along the thermal profile (50-700 °C) and an approximation of its degree of stability or refractoriness in the soil [5].

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OC-19

SYSTEMATIC EVALUATION OF THE METABOLOME OF POLAR COMPOUNDS IN TWO SEPSIS LIVER MODELS USING MULTIPLATFORM CHROMATOGRAPHIC TECHNIQUES COUPLED TO HIGH-RESOLUTION MASS SPECTROMETRY

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Cholestasis is a liver disease which can be triggered (among other mechanisms) by inflammatory damage resulting from systemic inflammation such as sepsis. There is a current and urgent need to increase our understanding of the molecular principles underlying the progressive deterioration of the liver to improve the therapeutic approaches.

Metabolomics offers the possibility to help in elucidating the dynamics of the disease and define the main factors throughout the progression of liver inflammation. There is a constraint however, because the most comprehensive metabolite coverage must include the key characteristics of the polar hepatic metabolome. CE-MS and HILIC-MS can provide both overlapping and complementary information, as some metabolites can be detected in both, whereas some metabolites can be detected only in one of them.

We used a sample treatment compatible with HILIC-MS and CE-MS as well as with other platforms (GC-MS & RP-LC-MS lipidomics). These treatments were applied in both positive and negative ionization modes. Our goal was to characterize the statistically relevant compounds in the metabolomic profiles of mouse livers. The mice were subjected to two sepsis models: intraperitoneal inoculation of lipopolysaccharide (LPS) from E. coli and fecal suspension (FSI). We compared these results to a control group inoculated with phosphate buffered saline (PBS). Compounds were annotated by their m/z (MS1) using CEU Mass Mediator (http://ceumass.eps.uspceu.es/mediator/), combined with the information provided by the analysis of 279 real standards (retention/migration time, MS/MS fragmentation, in-source fragmentation) in both techniques.

In comparison, both techniques offer a big amount of metabolic information about amino acids and their derivatives, polyamines, nucleic acids-related compounds (purine and pirimidine bases, nucleosides, nucleotides, and analogues), organic acids and carbohydrate-related compounds. HILIC-MS provided 10 times more features than CE-MS, but the annotation capabilities of CE-MS offered a more characterized profile (almost 20% features annotated). We have been able to find statistically relevant differences between both treatments and control, as well as some differences between both treatments.

Both techniques show advantages and disadvantages to be used as part of the multiplatform approach necessary to fulfill comprehensive metabolite coverage of our metabolomics study

OC-20

OCCURRENCE OF TIRE RUBBER ADDITIVES IN A NATURAL ENVIRONMENT CHARACTERIZED BY HIGH WHEEL TRAFFIC

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Tire Wear Particles (TWPs) are tiny debris generated by the friction between tires and the road surface. These particles include, among others, synthetic rubber, fillers, softeners, vulcanizing agents and additives. Specifically, tire rubber additives (TRAs) and their transformation products (TPs) have raised interest due to their possible toxicity to aquatic species [1]. Limited information is known regarding the presence and impacts of Tire Rubber Additives (TRAs) in the environment. Few studies have been conducted in Spain.

The aim of this study is to evaluate the impacts of these chemicals in the Llobregat River Delta (Catalonia, Spain), a natural protected space surrounded by densely-populated urban, agricultural and industrial areas and close to the second-biggest Spanish airport (that of Barcelona, in El Prat de Llobregat). Several samples including water, air and biota (fish and macroinvertebrates) have been collected in four sampling campaigns including dry and rainy periods between 2023 and 2024.

Water samples (n=75) were analyzed by liquid chromatography coupled to high resolution mass spectrometry (LC-HRMS). Preliminary data showed higher concentrations of several TRAs and TPs after rainy events, with concentrations that double those of the base level. Further monitoring of this area is needed to characterize environmental exposures to TRAs and TPs and assess the impacts of these chemicals into this natural protected area.

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OC-21

SIMPLIFIED METHODOLOGY FOR THE ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS METABOLITES IN URINE. EXPOSURE ASSESSMENT IN CHILDREN AND FIREFIGHTERS

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Polycyclic aromatic hydrocarbons (PAHs) are toxic organic compounds consisting of two to six fused benzene rings [1, 2]. These compounds are components of fossil fuels and unintentionally produced during incomplete combustion of organic materials, and are ubiquitous in the environment. Humans are exposed to PAHs essentially through inhalation of smoke and contaminated air, although ingestion of contaminated food (e.g., barbecued food), and industrial emissions, among others, are other exposure pathways [3]. Most individual PAH are classified by IARC [4] as probably carcinogenic to humans (group 2A), or possibly carcinogenic to humans after long-term exposure [4]. PAHs are metabolized in the liver producing hydroxylated metabolites (OH-PAHs), which are then easily excreted through urine. Therefore, urine is the simplest and least intrusive method to assess human exposure to PAHs [5]. This study is aimed to implement a methodology able to detect and quantify up to 16 OH-PAHs in urine samples. For this purpose, samples were liquid-liquid extracted followed by a derivatization step with BSTFA + 1% TMCS. Different sample volumes and extraction solvents were tested. Finally, the instrumental determination was performed by gas chromatography coupled to tandem mass spectrometry (GC-MS/MS), enduring a total analytical run of 27 minutes. The GC-MS/MS method has been validated in terms of accuracy, linearity and precision. The methodology has been externally validated by the analysis of samples from the German External Quality Assessment Scheme (G-EQUAS), encompassing two metabolites of naphthalene and one of pyrene. This methodology has been tested in urine samples from two population studies: 1) children from air pollution areas in Poland, and 2) firefighters in Spain during controlled forest burns, that can be exposed to high PAH concentrations [6]. This methodology is suitable for the assessment of human exposure to PAHs in vulnerable population groups including children from the general population and workers.

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OC-22

METABOLOMICS BASED ON LIQUID-CHROMATOGRAPHY-HIGH-RESOLUTION MASS SPECTROMETRY REVEALS KEY MARKERS TO AUTHENTICATE THE BOTANICAL ORIGIN OF HONEY

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Honey, a natural product produced by bees from flower nectar, is renowned for its distinct organoleptic properties, including its rich flavor, aroma, and varying colors and textures. There are different factors influencing the honey composition, including preharvest conditions, such as the botanical origin, that play an important role in the overall properties of honey (e.g., taste and aroma) [1]. Nowadays, honey remains a vulnerable food product since it can be mislabeled regarding its botanical source. In this context, this study introduces an innovative untargeted metabolomics approach using ultra-high performance liquid chromatography (UHPLC) coupled with quadrupole-Orbitrap-high-resolution mass spectrometry (HRMS) to reveal, for the first time, key compounds (markers) showing the influence of the botanical origin on the metabolomic composition of honey. Different supervised orthogonal partial least squares discriminant analysis (OPLS-DA) models were constructed based on UHPLC-HRMS honey fingerprints to differentiate between rosemary, orange blossom, and eucalyptus honey that were studied bearing in mind their wide use. The models demonstrated successful sample clustering, high-quality parameters ($R^2Y = 0.929$-0.981 and $Q^2 = 0.868$-0.952), and excellent predictability for external samples, with a full correct classification rate of 100%. Furthermore, this methodology enabled the putative identification of 12 significant metabolites, mainly described as amino acids and derivatives, serving as markers with high discriminant potential to distinguish between honey botanical origins. The findings highlighted key markers of eucalyptus *vs*. orange blossom honey such as *N*-(1-deoxy-1-fructosyl)proline, and raffinose or *L*-proline as markers of rosemary *vs*. orange blossom honey, among other key metabolites that could be used for botanical origin authentication purposes. This study opens the path to new metabolomics strategies to ensure the integrity of honey and other high-value foodstuffs, by addressing the identification of key significant compounds that have been scarcely studied until now.

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OC-23

OCCURRENCE OF WASTEWATER-DERIVED CONTAMINANTS IN TWO IRRIGATION WATER SYSTEMS, AND THEIR FATE INTO AGRICULTURAL SOILS: SPATIAL ANALYSIS AND SOIL RISK ASSESSMENT

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The need for irrigation-suitable water in regions with freshwater scarcity necessitates adequate wastewater treatment systems that do not pose a risk to agroecosystems. This includes addressing organic micropollutants commonly found in wastewater, such as pharmaceuticals. Along the Mediterranean region, several strategies are being developed to promote alternative water sources for agricultural purposes, such as reclaimed water. In this study, two alternative irrigation systems were considered for the irrigation of 2 agricultural plots planted with lettuce. The goals of the study involved the identification of the main wastewater-derived contaminants (WWDCs) occurring in the irrigation water, as well as those accumulated in the soils along two campaigns (fall and summer). For the analysis, a “target” approach considering 66 analytes was performed, with a quadrupole linear ion trap tandem mass spectrometry (UHPLC-QqLIT). To assess the fate of the continimants within the soil, three spatial dimensions were considered: the bulk soil, the rhizosphere soil (soil surrounding the roots), and the rhizoplane (the interphase between the soil and the roots). After the crop growth period, the bulk soil was collected in the space between the drippers and the plants. Once the plant was harvested, the rhizosphere soils were collected by shaking the roots. Finally, the roots were then soaked in a NaCl solution (RS), and the soil bonded to the roots interfae was collected in the solution, which finally was filtered to separate the solids. For the pharmaceutical analysis, ultrasound extraction and SPE were performed for the NS and BS soils. The RS solutions were extracted by SPE. Over 43 compounds were detected in the irrigation waters from the two treatments, and up to 33 of them were detected in soils at both campaigns. During the summer campaign, higher occurrence and concentrations were detected for the WWDCs in all the matrices. Diuretics, antihypertensives and non-steroideal analgesics and anti-inflammatories were among the more representative pharmaceuticals, while for other WWDCs, bisphenol A was among the most detected analytes. As for the soil, higher concentrations were found in the rhizosphere soils compared to the bulk soil. From the analytes detected in the rhizosphere soils, 9-25 were found in the rhizoplane, in contact with the roots. At the moment, and considering the soil parameters as the organic fraction, a soil risk assessment is being performed. To perform a comparison with the typical estimations made based on the water concentrations, the results obtained from the measured soil concentrations in the bulk and rhizosphere soils will be compared to the estimation based on the irrigation water concentrations. It is expected that this approach will provide further information on the accuracy of the currently used models for soil risk assessment.

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ORAL YOUNG RESEARCHERS COMMUNICATIONS

OY-01

CHEMICAL CHARACTERIZATION OF THE VALORIZED WINERY BY PRODUCT *VITIS VINIFERA* L. CV. TANNAT POMACE BY COMPREHENSIVE TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY (LC X LC)

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Numerous natural products have demonstrated therapeutic properties against various diseases due to the presence of various natural bioactive compounds like phenolic compounds. In this regard, the pomace of *Vitis vinifera* L. cv Tannat, the primary by-product of wine production, is particularly noteworthy. This is due to the Tannat variety is highly rich in phenolic compounds with potential bioactivity, mainly anthocyanidins (AN) and condensed tannins (CT), and the fact that a significant fraction of them remains in the pomace after vinification. However, analyzing some of these bioactive compounds by HPLC, and, in particular tannins, is especially challenging because of their immense chemical complexity, diversity and polymerization degree that results in coelution of different analytes in large unresolved peaks [1]. Therefore, the analysis of such compounds generally requires different preparation methods and/or the application of techniques that provide better separation capabilities, such as comprehensive two-dimensional liquid chromatography (LC x LC) [1].

This work aimed to develop an LC x LC-MS/MS method to analyze CT and AN in samples obtained from the valorization of grape (*Vitis vinifera* L. cv. Tannat) pomace by-product by green processes using pressurized liquid extraction. For the LC x LC method, C18, HILIC and PFP columns were assessed for the first dimension separation (^{1}D), while for the second dimension (^{2}D), different C18 columns were evaluated. The rest of the separation parameters (mobile phases for both dimensions, acids, sample solvent, gradients, modulation times and strategies for reducing the ^{1}D solvent strength [2]) were also deeply evaluated to maximize the resolution and separation capacity of the 2D method. Moreover, different methods of sample preparation were studied, including solid phase extraction, liquid-liquid extraction, and ultra-centrifuge filtration.

The optimized method resulted in a huge peak capacity and therefore it provided a maximized separation and identification power for a wide range of CT and AN from complex Tannat extracts, which is essential as a starting point for subsequent studies on biotransformation during digestion and potential beneficial health effects.

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OY-02

EXTRACTION OF SAFRANAL AND CROCINS FROM *Crocus sativus* USING NEOTERIC SOLVENTS

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Crocus sativus, known as saffron, is a natural source of bioactive carotenoids and terpenoids. Its main components are crocins and crocetin derived from zeaxanthin, picrocrocin and safranal, which give it its characteristic color, flavor and aroma (1). Their bioactive properties, such as cardioprotective, neuroprotective and anticarcinogenic effects, have been extensively studied (2).

Saffron based supplements are currently highly demanded. For their production, extracts of bioactive compounds are obtained using conventional solvents; however, their different chemical structures make their selective extraction a challenge. Recently, neoteric solvents, such as biomass-derived biosolvents (e.g. terpenoids) or natural deep eutectic solvents (NADES), have emerged as an interesting alternative to conventional solvents for their lower price, sustainability, better biocompatibility and solvent capacity (3). Therefore, in this work the use of different neoteric solvents for the extraction of bioactive compounds from saffron were investigated and the results were compared with conventional solvents.

Firstly, the COSMO-RS (Conductor-like Screening for Real Solvents) theory was applied to carry out an *in silico* screening of the potential solvents. Based on the chemical structure of the analytes, the program estimates the interactions they will have with respect to the solvents. The choice of the best neoteric solvents is made in relation to the solvent capacity and the grade of hydrophobicity for safranal and crocins. In this sense, NADES of different hydrophobicity based on thymol:verbenone, thymol:butanoic acid, choline chloride:glycerol and choline chloride:ethylenglycol, were selected and experimentally synthesized. Other biosolvents such as verbenone and carvacrol were also independently considered. Saffron extracts were obtained using NADES, biosolvents and conventional solvents (water and methanol:water, included for comparative purposes) under mechanical agitation at 45 °C. HPLC-DAD-MS analyses of the extracts revealed that the highest extraction yields of safranal and crocins were obtained using chloride:glycerol, with values of 3.35 and 134.83 mg g^{-1} respectively, above the 1.64 and 105.68 mg.g^{-1} achieved with water. The highly hydrophobic terpenoids employed gave lower yields, although carvacrol showed a much higher extraction selectivity towards safranal, with values of 2.15 mg g^{-1} for safranal and only 1.4 mg g^{-1} for crocins. In view of the results obtained, the aforementioned biosolvents could satisfactorily replace conventional organic solvents for the extraction of safranal and crocin from saffron, offering outstanding advantages such as high biodegradability, renewability and low toxicity.

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OY-03

UNTARGETED LIPIDOMICS BY UHPLC-IMS-QTOF MS FOR DIET INTAKE BIOMARKERS DISCOVERY IN *SPARUS AURATA* FISH

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Lipids play crucial roles in biology as essential components of cell membranes, signaling molecules and energy-storage substrates. The biological functions of lipids are determined by their structural diversity. Dietary changes can alter the lipidomic profile, resulting in either harmful or beneficial health effects (1). To understand the relationship between diet and health, biomarkers that accurately reflect the consumption of health-relevant foods are needed. Untargeted metabolomics can provide a more comprehensive image of dietary intake by measuring the lipidomic profile in biological samples. For biomarker detection is required a high selectivity and sensitivity, hence high resolution-mass spectrometry techniques (HRMS) are the most suitable option (2). The aim of this work was to study the lipidomic profiling of Sparus Aurata, one of the most consumed fish in the Mediterranean Sea, based on different diets, including fish, plants, byproducts or alternative ingredients. The sample extracts were analyzed by liquid chromatography (LC) coupled to ion mobility separation high-resolution mass spectrometry (IMS-HRMS), in both ionisation modes (ESI+/ESI-). After data processing and multivariate statistical analysis, a total of 35 markers, including phosphatidylcholines (PCs), phosphatidylethanolamines (PEs), and triacylglycerides (TAGs), among others, were annotated as distinctive features. The benefits of IMS in the identification of dietary biomarkers have been demonstrated by the use of collision cross section (CCS) values as an additional structural parameter. Preliminary results have shown a higher presence of triacylglycerides and diacylglycerides in the diet based on alternative ingredients. Health effects based on the presence or absence of these biomarkers are currently being studied.

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OY-04

ASSESSMENT OF PERSISTENT, MOBILE AND TOXIC COMPOUNDS UPTAKE IN ESCAROLE AND TOMATO PLANTS IRRIGATED WITH CONTAMINATED WATER IN A GREENHOUSE

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The reuse of wastewater for irrigation is presented as a strategy to address water scarcity. However, contaminants of emerging concern, particularly persistent, mobile and toxic (PMT) compounds, might be present in reclaimed water due to the inefficiency of wastewater treatment plants in removing certain pollutants. Therefore, irrigation of crops with contaminated water could lead to uptake by plants or soil [1].

The aim of this work was to understand the behaviour and the possible accumulation of selected PMTs in escarole, tomato plants and agricultural soil after irrigation with contaminated water in an experimental plot performed in a greenhouse. Eight PMTs were selected for this study: benzophenone-3, clarithromycin, imazalil, metformin, sulpiride, terbutryn, tiapride and tramadol. Three different irrigations were applied: i) control (Ctr), i.e., non-fortified water, ii) low fortification level (LF), water fortified at 0.5 µg L^{-1} and iii) high fortification level (HF), water fortified at 5 µg L^{-1}. The experimental plots were carried out following the distribution of *Latin squares*: three lines of plants were disposed in a different location each divided into 3 irrigation subgroups (Ctr, LF and HF) of 4 plants each. While escarole and tomato samples were collected at harvest time, soils and leaves were sampled at the beginning, in the middle and at the end of the harvest.

Samples were analyzed using a QuEChERS-based extraction method followed by mixed-mode liquid chromatography coupled to tandem mass spectrometry for the determination of the PMTs. As expected, in soil samples, the concentration of PMTs increased as the cultivation time progressed both in LF and HF irrigation (ranging from 5.2 to 225 ng g^{-1}). The results obtained for escarole showed that only tramadol was absorbed by the plant (1 ng g^{-1}). Whereas in tomato plants (neither in fruits nor in leaves) any PMT was observed. Furthermore, the plant physiological state was studied to elucidate whether the accumulation of PMTs induced stress in the escarole and tomato plants. Plant weight, photosynthetic and transpiration rates, chlorophyll content, and the levels of plant hormones involved in stress response, such as abscisic acid, were analysed.

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OY-05

STUDY OF WHEY PROTEINS AND CASEINS BEHAVIOUR IN A NADES AQUEOUS BIPHASIC SYSTEM. RESOLVING DISCREPANCIES IN UV AND CAPILLARY ELECTROPHORESIS RESULTS

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Milk is an abundant source of relevant varied proteins which can be classified depending on whether they are found into the whey protein fraction or the casein fraction. Different methods for concentrating and recovering them from dairy products and subproducts have been proposed. Taking into consideration the Green Analytical Chemistry principles, natural deep eutectic solvents (NADES) were evaluated by our group as part of an aqueous biphasic system (ABS) to study such proteins partition [1]. That study demonstrated the compatibility of the ABS made of a betaine-urea based NADES [2] and dipotassium hydrogen phosphate with the capillary electrophoresis – sodium dodecyl sulphate (CE-SDS) mode to study milk proteins recovered in the ABS fractions. Nevertheless, up until now the behaviour of individual proteins in the mentioned ABS has not been studied.

The objective of the present study is to understand the behaviour of whey and casein proteins in the betaine-urea/salt ABS. To this aim, the ABS partition of alpha-lactalbumin and beta-casein was analysed individually as representative proteins from the whey and the casein fractions, respectively. With that purpose the recovery yield of the proteins in the NADES rich phase and the salt rich phase was estimated by UV spectrophotometry and CE-SDS after solvent exchange to water.

The CE-SDS analyses showed that both proteins were mainly recovered in the NADES rich phase. Strikingly, these recovery rates from CE-SDS results perfectly correlated with the ones obtained with the spectrophotometer only for alpha-lactalbumin. The calculated beta-casein recovery rates based on CE-SDS analyses highly differed from the UV spectrophotometry results when using a beta-casein in water calibration curve. However, they were in agreement when the casein calibration curve for spectrophotometry contained a tiny amount of NADES. Deeper analysis of results suggested that traces of urea-containing NADES could remain after additives removal step avoiding beta-casein aggregation that would happen when dissolved in water. Opposite to UV spectrophotometry, CE-SDS leads to coherent results by employing casein in water calibration curve, most probably due to the SDS effect.

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OY-06

SUSTAINABLE RED SEAWEED BIOREFINERY: ULTRASOUND, PRESSURIZED LIQUID EXTRACTION, AND NATURAL DEEP EUTECTIC SOLVENTS INTEGRATION

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In recent years, there has been an increased interest in the study of high-value compounds from algae, especially in the development of innovative additives for the food and cosmetic industries. *Palmaria palmata*, commonly called “dulse,” is an edible seaweed characterized by its relatively high protein content (35% w/w) (especially phycobiliproteins), interesting sulfated polysaccharides, and its richness in phenolic compounds. The aim of this study was to develop an environmentally friendly extraction methodology to isolate phycobiliproteins, sulfated polysaccharides, and phenolic compounds from *Palmaria palmata*. The extraction process was carried out in three sequential steps using a combination of Pressurized Liquid Extraction (PLE) integrated with different Natural Deep Eutectic Solvents NaDES. The highest total protein, phycobiliprotein, and sulfated polysaccharide contents exerting the highest antioxidant capacity were obtained by using PLE in combination with glycerol:glucose (1:2) as NaDES in the first and second steps of the sequential process. Furthermore, a stability study of the optimal PLE-NaDES extracts was performed and compared with a PLE extract obtained using pure water instead of NaDES. The results indicated that PLE-NaDES extracts showed higher stability in preserving the phycobiliprotein color. Finally, phenolic compounds retained in the second step were recovered in a third step using PLE with NaDES composed of choline chloride:glycerol (1:2). The efficiency of PLE-NaDES extraction for the recovery of phenolic compounds was evaluated in comparison with a PLE extract obtained using 70% ethanol, demonstrating a higher capacity of chloride:glycerol (1:2) over ethanol. Overall, this study contributes to the recovery of high-value components from algae through sustainable and environmentally friendly methods offering an alternative approach in line with the principles of Green Chemistry.

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OY-07

OPTIMIZATION OF LARGE VOLUME SOLID PHASE EXTRACTION (LV-SPE) FOR TOXICOLOGICAL ASSESSMENT OF PHARMACEUTICALS IN TREATED WATERS FROM COSTA BRAVA

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The increasing presence of pharmaceuticals in aquatic environments has raised concerns about their potential effects on wildlife and human health. This study focuses on the optimization of extraction procedures for large volumes of treated waters, specifically from secondary and tertiary treatments from Water Regeneration Stations (ERAs) across Costa Brava. Firstly, a small portion of water samples collected was analyzed by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) in order to identify residues of pharmaceuticals. Moreover, to evaluate the ecological impact, the extracted samples were preconcentrated x5 and x20 and exposed to *Daphnia magna*, a model organism in ecotoxicological studies. Behavioral changes in *Daphnia magna* were monitored to assess toxicity.

On the other hand, a targeted metabolomic study (LC-MS/MS) was conducted on pooled samples of five *Daphnia magna* individuals to identify biochemical changes induced by extracts exposure. Partial Least Squares (PLS) regression was employed to correlate pharmaceutical concentrations with observed behavioral changes, highlighting compounds with the highest selectivity ratios for each test. The robustness of these correlations was further validated using the metabolomic results, focusing on neurotransmitters routes.

Our findings underscore the importance of combining advanced chromatographic techniques with toxicological and metabolomic analyses to evaluate the environmental impact of pharmaceuticals. This multidisciplinary approach offers valuable insights for environmental monitoring and the development of strategies to mitigate the effects of pharmaceutical contaminants in aquatic ecosystems.

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OY-08

TRANSIT AND BIOCONVERSION OF POLYPHENOLS IN THE DIGESTIVE AND CIRCULATORY SYSTEMS OF BROILERS FED ON GRAPE MARC-FEED

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The agri-food and livestock sector are facing an increasing demand for resources, competing with each other to satisfy the need for food and feed production. In this competition for common raw materials, the incorporation of by-products from the food sector into feedstuff emerges as a potential alternative to reduce this pressure. In addition, current regulations require that the origin of these functional ingredients for animal feed must be of high quality and prioritise animal welfare. The effective addition of these functional by-products can also respond to another challenge of the sector, through the prevention or alternative treatment of pathologies, instead of the traditional use of antibiotics, due to the worrying antimicrobial resistance (AMR). In this context, this work focuses on the reuse of the main by-product of the wine industry, grape marc, for the functional enrichment of broiler diets. Using a patented extraction process, a solid extract rich in phenolic compounds is generated from grape marc. Its effectiveness is evaluated by means of a dosage study, incorporating 0 ppm (T1, control), 750 ppm (T2) and 1500 ppm (T3) levels of total polyphenols in the feed of these birds. The *in vivo* study was carried out with 240 broilers (n=240) separated into groups of 20 birds per pen, with 4 pens per level. In addition, to evaluate the effect of the solid extract on animals experiencing enteric stress, two additional groups were challenged (n=80 each) by a common parasitic condition in poultry, evaluating the effect of the maximum addition of the extract (T5) in contrast to the infected control group fed with a base diet (T4). The analysis was carried out by evaluating the digestive tract and circulatory system of these animals, incorporating samples from crop, caecum and serum of the broilers. Extractions of the biological samples were carried out using the solid-phase matrix dispersion (MSPD) technique and analysed by HPLC-MS/MS for the targeted detection of phenolic markers, in both base and fortified feeds, as well as in biological samples from control and experimental groups. In addition, a non-targeted analysis by UHPLC-QTOF was performed, incorporating various statistical analyses for the segmentation and grouping of the different levels of addition in feed and biological specimens, in order to detect potential effects generated by the addition of the extract. The results show a clear transfer of phenolic compounds to the broilers digestive tract. Several phenolic bioconversion derivatives have been also detected as bacterial metabolites, revealing a significant impact on the welfare of these animals.

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OY-09

DETERMINATION OF HIGH PRODUCTION VOLUME CHEMICALS AND POLYCYCLIC AROMATIC HYDROCARBONS IN PARTICULATE MATTER BY THERMAL DESORPTION COUPLED TO GAS CHROMATOGRAPHY AND MASS SPECTROMETRY

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High production volume chemicals (HPVCs) and polycyclic aromatic hydrocarbons (PAHs) are two of the groups of semi-volatile organic compounds which can be found in an equilibrium between the gas phase and the particulate matter found in air. They can enter the human bloodstream through the inhalation of these particles, leading to health problems such as an increase in cancer risk or respiratory damage [1],[2].

This work aims to study the viability of thermal desorption (TD) as a desorption technique for their determination in <10 µm particulate matter (PM10) retained in quartz fibre filters (QFFs), as opposed to the popularly employed desorption techniques using organic solvents [2],[3],[4].

A direct multi-residue method based on TD-GC-MS was developed and validated for the determination of 24 HPVCs and 13 PAHs in PM10 at pg m-3 concentrations. The use of TD yielded similar sensitivity to the one obtained with organic solvent desorption techniques, although some of the originally targeted compounds could not be determined. This could be due to the design of the used instrumentation, which has a long transfer line between the TD and the GC, or due to thermal decomposition. PM10 samples collected in the Port of Tarragona (Spain) were analysed, with the most abundant compounds being the phthalate esters (PAEs).

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OY-10

ANALYTICAL APPROACH FOR DETERMINATION OF TIRE RUBBER ADDITIVES AND THEIR TRANSFORMATION PRODUCTS IN SILICONE BANDS

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Tire Wear Particles (TWPs) are a consequence of the friction of the tread on the asphalt during vehicle circulation and they are increasingly recognized as important sources of contamination of different environmental compartments such as air, soil, water and biota. Associated with the TWPs are numerous tire rubber additives (TRAs), mostly antioxidants that are commonly added to rubber to improve performance and delay ageing which have been highlighted for their potential toxicity [1].

Due to adverse weather conditions, these compounds undergo different processes such as such as photochemical oxidation, thermal degradation and biodegradation that change the chemical composition of additives leading to the formation of Transformation Products (TPs) can have even more devastating effects on the environment [2].

Human exposure to Tire wear particles and associated additives primarily occurs through inhalation, with potential additional routes via dermal contact and ingestion of contaminated food or water [2]. This project aims to develop an analytical methodology to extract and quantify TRAs and TPs in silicone bands. This methodology was employed in the analysis of silicone bands worn by adolescents and their family members during one week, as well as silicone patches placed around their municipality. Silicone bands and patches allowed to assess exposure levels and perform health risk evaluations, as silicone bands are increasingly recognized as a useful tool to monitor dermal exposure [3].

Initial studies have focused on the optimization of sample preparation workflows, including extraction time, number of extractions, and solvent volumes. Instrumental analysis using Liquid Chromatography coupled with tandem Mass Spectrometry (LC-MS/MS) employed a tailored method targeting 50 common TRAs and TPs, encompassing N,N'-substituted p-phenylenediamines (PPDs), benzothiazoles, benzotriazoles, and cyclic amines. Preliminary data from healthy volunteers indicate elevated concentrations of benzothiazoles in silicone bands, ranging from 2 to 16 ng/g

This study underscores the importance of investigating tire related contaminants, providing insights into exposure pathways and potential health risks associated with these ubiquitous environmental pollutants.

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POSTERS

P01

UPGRADING AN ANALYTICAL METHOD FOR THE DETERMINATION OF PMT AND vPvM SUBSTANCES IN GROUNDWATER

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In recent years, the occurrence of persistent, mobile, and toxic (PMT) and very persistent and very mobile (vPvM) substances in various water sources has gained importance within the scientific community as they could pose a risk to environmental and human health. In fact, the German Environment Agency has established criteria to identify PMT and vPvM substances under the EU chemicals regulation REACH (EC 1907/2006 Registration, Evaluation, Authorization and Restriction of Chemicals). It is acknowledged that PMTs are compounds commonly found in water environment. Several studies in Europe have reported concentrations of PMTs range from ng L−1 to µg L−1 in aquatic environments [1].

The potential mobility of these contaminants toward groundwater has triggered the need to identify and prioritize them for their potential inclusion in surveillance lists. In this context, the objective of this work is to upgrade a multi-residue analytical method for the determination of PMT and vPvM substances in groundwaters, based on the method developed by Montes et al. [2]. For contaminants preconcentration, three different solid phase extraction (SPE) methods were evaluated to determine the optimal water pretreatment step. The first method used mixed-mode WAX and WCX SPE cartridges, another used Oasis HLB cartridges, all of them are from Waters Corporation, while the third used custom-made cartridges. For quantitative analysis, Ultra High-Performance Mixed-Mode Liquid Chromatography coupled with tandem mass spectrometry (UHPLC-MS/MS) was used. New compounds, such as Benzophenone-3, Guanylurea, and Melamine, were added to the Montes et al. analytes list, resulting in a total of 48 PMT compounds analyzed.

The methodology was applied to the determination of these 48 PMT and vPvM compounds in samples collected by the Catalan Water Agency (ACA) in various municipalities in Catalonia along the Llobregat River Basin and associated aquifer. The goal is to identify the most relevant compounds within this group of substances and generate novel insights on their occurrence in the Catalonia region.

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P02

UNDERSTANDING THE PARTITION OF SOLUTES IN COLUMNS THAT MIMIC BIOLOGICAL PROCESSES THROUGH THE ABRAHAM SOLVATION PARAMETER MODEL

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Biomimetic chromatography is nowadays gaining relevance due to the growing interest in evaluating parameters related to biological processes in a high-throughput manner. Therefore, some years ago columns with human serum albumin (HSA) and alpha-1-acid-glycoprotein (AGP) covalently bonded to a chromatographic support were developed as stationary phases. Both HSA and AGP act as drug carriers in blood and, hence, drug-protein binding rules properties such as drug distribution and bioavailability. The retention of compounds in protein-based columns is closely related to the *in vivo* protein binding, and the measurement of the retention in these columns would help to characterize protein binding not only in a high-throughput manner but also reducing the number of *in vivo* experiments during the drug development process in pharmaceutical industry.

A model widely used to study the interactions that rule chromatographic partition is the solvation parameter model, developed by M. H. Abraham in the early nineties [1]. This model, based on linear free energy relationships, explains the partition of neutral compounds between the two chromatographic phases through five terms (Eq. 1), related to the ease of creating a cavity in the solvent to allocate the solute (v V term), hydrogen bonding interactions (a A and b B), and dipole and induced dipole interactions (e E and s S terms). Some years later, a new model with two additional terms ($j^+ J^+$ and $j^- J^-$) was proposed to also consider the partition of ionizable compounds [2]. Therefore, Eq. 1 can be applied to characterize the main interactions that rule the retention of neutral compounds in chromatographic systems, whereas Eq. 2 explains the retention of neutral and ionic compounds.

$$\log k = c + e\,E + s\,S + a\,A + b\,B + v\,V \qquad \text{(Eq. 1)}$$

$$\log k = c + e\,E + s\,S + a\,A + b\,B + v\,V + j^+ J^+ + j^- J^- \qquad \text{(Eq. 2)}$$

In both equations, *k* is the chromatographic retention factor of the compounds in the systems of interest. In the present work both models have been applied to HSA and AGP chromatographic columns. Results demonstrate that neutral compounds interact similarly to both proteins, although AGP has more affinity than HSA for compounds with strong hydrogen-bond basicity. Regarding ionic compounds, HSA shows higher affinity than AGP for anions, whereas the cations bind much more strongly to AGP.

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P03

CHROMATOGRAPHIC SELECTIVITY IN REVERSED PHASE AND HILIC COLUMNS

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Hidrophilic interaction liquid chromatography (HILIC) has attracted much more interest in the last few years as it is generally assumed to be complementary to reversed-phase liquid chromatography (RPLC). However, in HILIC we find a wide variety of stationary phases (bare silica; zwitterionic, diol, pentahydroxy, aminopropyl…) that, according to manufacturers, provide different chromatographic selectivities. Additionally, the column matrix (fully or superficially porus particle, monolithic) can also play a role in selectivity.

In this work a RPLC (XBridge C18), a pentafluorophenyl (Ascentis Express F5) and several HILIC columns (Chromolith Performance SI, ZIC-HILIC, ZIC-cHILIC, Chromolith Diol, LiChrospher 100 Diol, Purospher STAR NH2) have been characterized using a recently developed fast method [1] based on the Abraham's solvation parameter model ($\log k = c + e \cdot E + s \cdot S + a \cdot A + b \cdot B + v \cdot V$). From the injection of four pairs of compounds and four *n*-alkyl ketones with well-known molecular descriptors (E, S, A, B and V), it is possible to obtain information about the extent in the chromatographic system of solute-solvent polarizability and dipolarity interactions (e, s), solute hydrogen bonding acidity (a) and basicity (b), and the easiness of the formation of a cavity in the chromatographic phases to accommodate the solute (v), which are the main interactions affecting retention and therefore selectivity.

The obtained results show that interactions in HILIC are almost reversed to those in RPLC, confirming the assumed complementarity between these chromatographic modes, and the pentafluorophenyl column behaved more similarly to RPLC than HILIC. Differences in column length, particle diameter or porosity change the strength of the interactions, but not the relative particular selectivities (cavity formation, dipolarity/polarizability, and acidity/basicity hydrogen bonding). Finally, the selection of the mobile phase organic modifier in HILIC has a more significant impact on selectivity than the stationary phase.

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P04

BIOMIMETIC CHROMATOGRAPHY: CHARACTERIZATION OF MICELLAR AND MICROEMULSION ELECTROKINETIC SYSTEMS BY A FAST LFER APPROACH

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In drug discovery and environmental protection there is an increasing interest in the surrogation of biological processes by means of physicochemical systems, in particular chromatographic systems. In those processes where there is a distribution of bioactive compounds between two different media (i.e. gastrointestinal fluids and the intestinal barrier, or water and soil), biomimetic chromatography has revealed as a very promising alternative to animal experimentation. However, finding a suitable chromatographic biomimetic surrogate requires a careful characterization of both the biological and chromatographic systems and a favorable comparison.

The Abraham's LFER model allows to elucidate the contribution of different solute-solvent interactions to solvation related properties (*SP*, such as chromatographic or biological parameter), according to the following general equation for neutral compounds [1]:

$$\log SP = c + e\cdot E + s\cdot S + a\cdot A + b\cdot B + v\cdot V$$

where the terms $e\cdot E$ and $s\cdot S$ account for polarizability and dipolarity interactions, $a\cdot A$ and $b\cdot B$ for hydrogen bonding, $v\cdot V$ for the cavity formation in the solvent to accommodate the solute. The uppercase letters of these terms represent solute molecular descriptors, and the lowercase ones are the system coefficients characterizing the selectivity of the chromatographic (or biological) system. c is a constant term, mainly related to the phase ratio in HPLC. However, the conventional application of this characterization method is time-consuming, since it involves the analysis by multilinear regression of a considerably high number of compounds.

Micellar and microemulsion electrokinetic chromatography systems appear to be a very interesting biomimetic option due to their easiness of tuneability (buffer and pH, surfactant, organic solvent…). In this work we have adapted a fast method recently developed for liquid chromatography [2] to the characterization of electrokinetic systems. In the proposed methodology, the micellar/microemulsion marker and the v coefficient are determined from the injection of a few *n*-alkyl phenone homologues, and e, s, a and b are rapidly measured from the mass distribution ratios of carefully selected pairs of compounds.

The comparison of the Abraham's coefficients of a good number of biological and chromatographic systems is an interesting tool to identify promising biomimetic surrogates.

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P05

L-ARGININE BASED CHIRAL IONIC LIQUIDS FOR THE ENANTIOMERIC ANALYSIS OF AMINO ACIDS BY ELECTROKINETIC CHROMATOGRAPHY AND LIGAND EXCHANGE CAPILLARY ELECTROPHORESIS. A COMPARATIVE STUDY

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Amino acid-based ionic liquids (AAILs) have demonstrated in the last years a high potential to achieve the enantiomeric separation of different chiral compounds [1]. They can be divided into i) AAILs in which protein amino acids are the anionic counterpart and ii) AAILs in which amino acids are the cationic counterpart. In the field of chiral separations, the use of these AAILs has been described in electrokinetic chromatography (EKC) systems combined with cyclodextrins or in the mode of ligand exchange capillary electrophoresis (LECE). These chiral systems have mainly been employed for the enantioseparation of model drugs and to a lesser extent for amino acids analysis. However, since protein amino acids are the elemental piece for peptide and protein conformation and play an important role in the metabolic pathways, their enantiomeric determination is a challenge in the field of chiral separations.

In this context, this work aimed to perform a comparative study of the potential of different L-arginine-based ionic liquids, some of them synthesized for the first time in this work; for the chiral separation of five model amino acids (tryptophan, phenylalanine, valine, norvaline, and alloisoleucine) under two different CE modes: EKC and LECE. In the first case, AAILs containing bis(trifluoromethane)sulfonimide (NTf_2) as anionic counterpart were combined with different cyclodextrins, whereas in the LECE systems AAILs constituted by tetraalkylammonium (TMA) as cationic counterpart participated in the ligand exchange mechanism, forming ternary complexes with the chiral analyte and metallic cations. Under the most favorable conditions, the results demonstrated that the LECE mode based on the use of L-Arg-TMA with Cu (II) enabled the chiral separation of three out of the five amino acids studied (norvaline, citrulline, and phenylalanine). Finally, to demonstrate the potential of the developed LECE methodology, its analytical characteristics were evaluated, and it was applied to the enantiomeric determination of norvaline in dietary supplements.

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P06

GLOBAL VERSUS INDIVIDUAL MODELS TO DESCRIBE RETENTION WITH ISOCRATIC AND GRADIENT EXPERIMENTS IN RPLC

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Retention is the key property for governing HPLC resolution. It is influenced by several experimental factors, including the nature of the stationary phase, the mobile phase composition and acidity, flow rate, or temperature [1]. For simple and moderately complex samples, separation performance can be accurately predicted using chromatographic models. Conventional methodologies involve fitting each sample constituent to dedicated models (i.e., "individual retention models"), using data from carefully designed experiments typically involving injections of isolated standards. Recently, we developed an alternative paradigm for complex samples: "global retention models", which describe the behaviour of several constituents simultaneously [2–4]. These models distinguish between solute-specific retention contributions and those common to the column and solvent. Global models allow optimising resolution of full chromatograms with multiple peaks in complex samples, without needing standards or detailed knowledge of the peak identities. Global modelling reduces the number of model parameters, which is highly advantageous. Unlike individual models, a global model can be extended to incorporate new solutes by performing just one additional experiment. In this work, we compare the performance of individual and global models using both isocratic and gradient experimental designs for a set of 15 sulphonamides, analysed with three columns of different nature: C18, phenyl, and cyano. Parameters obtained with the Neue-Kuss in several scenarios are compared. This study highlights the efficiency and flexibility of global retention models in optimizing chromatographic separations for complex mixtures.

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P07

USE OF INDIVIDUAL AND GLOBAL RETENTION MODELS IN SERIAL COUPLING OF COLUMNS FOR ENHANCED SELECTIVITY IN RPLC

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Liquid chromatography has evolved significantly since its introduction in the 70s, with RPLC becoming the primary method for separating non-volatile compounds. The limited versatility of conventional stationary phases has driven the development of alternative techniques, such as the serial coupling of columns [1]. This approach integrates segments of specific nature and length to create hybrid configurations, significantly broadening the range of chromatographic selectivity, and improving separation efficiency while reducing analysis time. Advancements in column connection technologies, such as "zero dead volume" connectors, have facilitated its practical implementation [2]. This research explores the potential of column-coupling to enhance separation performance for a set of 15 probe compounds (sulphonamides of varying polarity), using binary or ternary combinations of C18, phenyl and cyano columns in both isocratic and gradient experiments. An interpretive methodology incorporating global retention and peak shape models for optimising chromatographic separations, peak purity as the objective function, genetic algorithms and Pareto plots for visualising separation performance [3,4], was applied. This approach enabled the identification of the optimal column combination and the best gradient or isocratic condition. The main objective was to investigate the benefits and limitations of global models compared to individual ones in column-coupling. The findings revealed that global models are fully suited for predictions. In addition, while cyano and phenyl columns alone failed to resolve the mixture, their combination significantly improved separation performance, due to their complementary selectivity.

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P08

COMBINATION OF SODIUM DODECYLSULFATE AND 1-HEXYL-3-METHYLIMIDAZOLIUM CHLORIDE AS MOBILE PHASE ADDITIVES

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Reversed-phase liquid chromatography (RPLC) relies on the combined use of a non-polar stationary phase and a more polar hydro-organic mobile phase. The retention of compounds is primarily influenced by their hydrophobicity, with more hydrophobic compounds being retained longer. However, ionic interactions between positively charged analytes and the anionic free silanol groups present in the stationary phase can significantly increase retention and cause tailing peaks in chromatograms [1]. To address these issues, mobile phase additives such as anionic surfactants and ionic liquids are used to introduce secondary equilibria in the chromatographic column, adjusting separation selectivity [2,3]. The combination of hydrophobic and electrostatic interactions between analytes and additives results in mixed retention mechanisms affecting elution. This study investigates aqueous chromatographic systems containing both the anionic surfactant sodium dodecyl sulphate (SDS) and the ionic liquid 1-hexyl-3-methylimidazolium chloride as mobile phase reagents, eliminating the need of organic solvents, buffered at pH 3.0 with a phosphate system. This leads to a highly sustainable HPLC procedure. The behaviour was examined with two different C18 columns (Zorbax Eclipse and XTerra-MS) to evaluate the strength of solute interactions through the calculation of equilibrium parameters and hydrophobic and electrostatic contributions, using simple mathematical models [4,5]. Focusing on the retention of six basic drugs (β-adrenoceptor antagonists), the study revealed the significant influence of electrostatic interactions. The feasibility of using aqueous systems combining SDS and an ionic liquid without organic solvents, to efficiently separate basic polar compounds with satisfactory resolution, is also demonstrated.

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P09

APPLICATION OF THE THEORY OF SOLUBILITY OF HANSEN TO THE SELECTION OF GREEN SOLVENTS FOR THE SELECTIVE EXTRACTION OF POLYCHLORINATED BIPHENYLS FROM COMPLEX BIOTIC SAMPLES

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Polychlorinated biphenyls (PCBs) are persistent organic pollutants that have extensively been used by industry in the past. Their introduction into the food webs is a cause of concern due to their toxicity and it makes the regular monitoring of their levels in foodstuffs mandatory to verify that concentrations remain below the maximum residue levels set in current legislation [1,2].

This study aims to propose eco-sustainable solvent(s) aligned with the principles of Green Analytical Chemistry [3] and Green Sample Preparation [4] as alternatives to the volatile, organic and toxic solvents obtained from fossil sources in use for this type of analytical determination. To achieve this goal, and using PCB 138 as model compound and extra virgin olive oil as model fatty matrix, the Theory of Solubility of Hansen has been used to identify green solvents that could potentially be used for the selective extraction of PCBs from fat-containing matrices. Two sustainable solvents appear to meet the required criteria: cyrene and the natural deep eutectic solvent thymol:vanillin (1:1).

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P10

NATURAL EUTECTIC SOLVENT SCREENING BY COSMO-RS FOR THE SELECTIVE BISPHENOL EXTRACTION FROM SOFT DRINKS

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Bisphenols are used in the epoxy resin lining of drinking cans to prevent corrosion and contamination of the content. However, these chemicals can leach into the beverage, especially under conditions of high temperature or prolonged storage. Intake of bisphenols, particularly bisphenol A (BPA), is linked to various health issues, including hormonal disruptions, reproductive harm, and increased risk of certain cancers. Regulatory efforts to limit BPA exposure have promoted the use of other bisphenol alternatives that must also be controlled. In this context, it is necessary to implement fast and reliable analytical methods to monitor bisphenol concentrations in foodstuffs as susceptible to their presence as canned soft drinks. To face this regulatory and social demand, the scientific community is currently focused on developing more environmentally friendly and sustainable methods, aligning with the principles of Green Analytical Chemistry.

Thus, the objective of this work was to evaluate the use of the Conductor-like Screening Model for Real Solvents (COSMO-RS) theory for the selection of those hydrophobic natural deep eutectic solvents (NADESs) with improved selectivity for a green liquid-liquid extraction (LLE) of bisphenols from sweetened soft drinks.

More than 30 NADESs were screened and the *in silico* approach indicated that both eucalyptol:1-dodecanol and eucalyptol:dodecanoic acid NADESs exhibited the highest selectivity of bisphenols over the typical sugars found in soft drinks (i.e., glucose, fructose, and sucrose). Additionally, the simulations indicated that the interface behavior of water/NADES is characterized by very low interfacial tension values, which facilitate mass transfer and, consequently, fast LLE processes. Both NADESs were prepared in the laboratory and characterized through their IR and NMR spectra, as well as by differential scanning calorimetry (DSC). Finally, vortex-assisted LLE was carried out under generic, non-optimized, conditions (1:5 NADES:sample ratio; 1 min) using both NADESs to experimentally test the performance predicted by COSMO-RS. Experimental results demonstrated good recoveries for bisphenols and high selectivity against sugars, as predicted by COSMO-RS.

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P11

EFFICIENT REMOVAL OF NATURAL DEEP EUTECTIC SOLVENTS IN EXTRACTS: ENHANCING PURITY AND BIOACTIVITY OF BIOACTIVE COMPOUNDS

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Despite their promising extraction capabilities, NaDES present challenges due to their low volatility which made them impossible to be evaporated from the extract, and their potential toxicity [1]. The objective of this work was to develop different strategies to efficiently remove NaDES from natural extracts and biomass residues while maintaining high yields and bioactivity.

To do that, two purification techniques were evaluated post-extraction after the application of an hydrophilic NaDES and supercritical CO_2 to recover natural bioactive compounds from citrus by-products: i) Solid-Phase Extraction (SPE) with C18 stationary phase cartridges and, ii) active charcoal suspension with magnetic stirring. The latter, proposed for its potential to increase terpene extraction yield, involved destabilizing NaDES with water, followed by active charcoal addition and stirring. Elution solvents included AcEt:MetOH (1:1,*v/v*) and EtOH:H_2O (1:1,*v/v*) mixtures. For the treatment of residues, an anti-solvent extraction method using EtOH and acetone washing steps was employed [2].

The active charcoal method provided better results than SPE, in particular the greener alternative using EtOH:H_2O retained 15% more carotenoids, 31.5% more terpenoids, and 12% more phenolic compounds than the AcEt:MetOH protocol. NaDES-free extracts showed high neuroprotective activity, measured by their antioxidant, anticholinergic and anti-inflammatory activities.

The application of the antisolvent method for the recovery of bioactive compounds from the biomass residues provided similar activity for the two different cleaning solvents (acetone and ethanol), indicating an effective NaDES removal with a significant reduction of the use of toxic solvents. The fractions underwent FT-IR analysis, which revealed specific signals indicating the disappearance of NaDES in all studied cleaning procedures. These results support the capacity of the studied techniques to destabilize NaDES and substantially reduce their content in the final bioactive product, mitigating toxicity concerns.

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P12

Comprehensive analysis of pesticide and fungicide levels in air and urine samples in agricultural areas. Pilot study.

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This pilot study examines pesticide and fungicide exposure dynamics in agricultural environments using air and urine sampling. Air sampling revealed application-related trends in compound presence, suggesting influences from agricultural activities and environmental factors. Compounds such as tetrahydrophthalimide, tebuconazole, captan, chlorpyrifos, carbofuran, and deltamethrin exhibited varied levels, potentially linked to spraying schedules and environmental conditions affecting their volatility and distribution.

Urine sampling data showed significant increases in specific biomarkers post-exposure compared to pre-exposure levels, indicating direct exposure to pesticides and fungicides among volunteers. DEAMPY, TCPY, TEB-OH, and 3-PBA levels notably increased post-exposure, highlighting the recent contact with these chemicals. Temporal analysis of urine samples demonstrated a gradual decrease in compound concentrations over subsequent days, reflecting the body's natural metabolism and elimination processes following exposure.

The integration of air and urine sampling provides a comprehensive assessment of exposure dynamics: air sampling identifies environmental presence and variability, while urine sampling quantifies individual uptake and elimination rates. This dual approach highlights the importance of monitoring both environmental levels and human biomarkers to accurately assess exposure risks and develop targeted mitigation strategies.

The results show the relationship between environmental exposure and human biomarker response in an agricultural setting. Understanding these dynamics is crucial for implementing effective measures to reduce exposure risks and protect the health of individuals exposed to pesticides and fungicides in agricultural environments.

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P13

HYPERCROSSLINKED SULFONATED CORE SHELL PARTICLES FOR THE SELECTIVE EXTRACTION OF PHARMACEUTICALS IN ENVIRONMENTAL SAMPLES

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Packing materials based on core shell particles (non-porous core surrounded with a porous shell) offers a series of advantages when applied mainly for chromatographic columns [1], but have scarcely used in sportive extraction techniques. Only some approaches have been already presented in the preparation of molecularly imprinted polymers with different core materials such as silica, magnetic nanoparticles or quantum dots [2].

In the present study, a homemade hypercrosslinked sulfonated core shell sorbent has been developed via a two-step polymerisation precipitation that delivers divinylbenzene core microspheres that then were subjected to hypercrosslinking and sulfonation reactions. Thus, this core shell material can simultaneously present reversed-phase and cation-exchange interactions (sulfonated groups in the shell) and act as an efficient mixed-mode ion-exchange sorbent [3]. The hypercrosslinked sulfonated core shells were applied in solid-phase extraction (SPE) of five basic pharmaceuticals from river, effluent wastewater and influent wastewater samples followed by liquid chromatography high resolution mass spectrometry (LC-HRMS).

With an optimised SPE protocol that promotes the selectivity, recoveries higher than 70% for all the compounds were obtained after loading 100 mL of ultrapure water sample, whereas similar recoveries were obtained when a non-core shell material [4] were used to upload 50 mL of ultrapure water, fact that highlight the importance in the particle morphology in the extraction.

The method using the core shell particles in SPE/LC-HRMS was also validated with apparent recoveries between 44 and 108%, matrix effect ranging from -24 to +25 in all complex matrices, and limits of detection of the low ng/L. Finally, the method was applied to the analysis of the studied environmental water samples and most of the pharmaceuticals were found.

Acknowledgements

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P14

UNVEILING THE ROLE OF CHAR INCORPORATED IN A POLI ε-CAPROLACTONE POLYMER THIN FILM FOR STEROID HORMONES MICROEXTRACTION

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Thin film microextraction (TF-ME) has emerged as an alternative to conventional extraction techniques used in sample preparation for analytical purposes. The thin film methodology offers several advantages compared to solvent extraction or solid-phase extraction, such as the use of small amount of reagents, materials and organic solvents for preparing the extraction phase, increasing the greenness of the technique. In previous works, we developed TF-ME methodologies for several types of organic pollutants (pesticides, personal care products, steroid hormones) using cellulose triacetate (CTA) as the polymer, and either solid or liquid modifiers as the active component [1-3]. Now, we move one step further to increase the sustainability of the TF-ME process by using poli ε-caprolactone (PCL) as the polymer (a biodegradable linear polyester derived from caprolactone monomer) together with different types of char as the extracting phase. The investigated sorbents were C1 (activated with H_3PO_4, high percentage of pores >1 µm, specific surface area (S_{BET}) = 2170 $m^2 \cdot g^{-1}$), C2 (activated with H_3PO_4, intermediate percentage of pores >1 µm, S_{BET} = 2190 $m^2 \cdot g^{-1}$), and C3 (activated through steam, low percentage of pores >1 µm, S_{BET} = 1114 $m^2 \cdot g^{-1}$). The target analytes were sex steroid hormones and HPLC-MS/MS analysis was performed.

Films were prepared using the solvent casting method in a ceramic mold (3.6 cm). Initial tests were performed to find out the most convenient solvent for the PCL dissolution (chloroform or acetic acid). Improved extraction performance of steroid hormones was obtained using the membrane prepared with chloroform as the solvent and with the addition of the char directly into the polymer solution (without using ethanol for the dispersion) [3]. Regarding the extraction kinetics (until 24 h, 40 mL tap water spiked at 50 µg L^{-1}), no significant differences were observed between the neat membrane (100% PCL) and the ones with C3. In contrast, the presence of C1 or C2, up to 30% w/w, significantly improved the extraction efficiency (>60% after 4h) compared to neat PCL films. The differences between the chars may be attributed to a larger S_{BET} and to the presence of larger pores in the case of C1 and C2. For PCL/C1 and PCL/C2 membranes, elution step (2 mL ethanol) provided recoveries around 30-75% and 40-98%, respectively.

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P15

COMPUTATIONAL ASSESSMENT OF MONOTERPENOIDS FOR A SUSTAINABLE REMEDIATION OF SULFONAMIDES IN WATER

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Sulfonamides are a class of synthetic antimicrobial agents that are widely used in both, human and veterinary medicine. Due to their extensive use, these compounds frequently enter aquatic environments, potentially leading to adverse ecological and health effects. Numerous techniques are available for eliminating sulfonamides from water sources, including biodegradation and sorption; however, research on environmentally friendly liquid-liquid extraction methods is still in its early stages. This can be mainly attributed to the abundance of potential solvents and the substantial experimental work necessary for their evaluation. Computational strategies, such as the Conductor-like Screening Model for Real Solvents (COSMO-RS), has emerged as a cost-efficient and effective option for solvent choice.

Thus, this research aimed to apply the COSMO-RS theory to find the most promising monoterpenoids for the development of an environmentally friendly and sustainable remediation process for sulfonamide-contaminated water (sulfadimethoxine, sulfadimidine, sulfamethoxazole, sulfamethoxypyridazine, sulfadiazine, and sulfaquinoxaline), identifying the main interaction forces involved in the extraction process.

The acid/base behavior of the studied sulfonamides indicated that at pH 7, their predominant states are neutral and deprotonated. This suggested that the use of hydrophobic extractants for their removal from aqueous matrices may be a viable approach. Moreover, their σ-profile provided further evidence to support this argument, indicating that sulfonamides are capable of establishing not only hydrogen bonding interactions but also exhibiting a high potential for hydrophobic and electrostatic interactions. These findings led to the evaluation of the solvent capacity of a set of 116 hydrophobic monoterpenoids with varying functionalities against sulfonamides in their neutral state, identifying citral, carvacrol, and verbenone as the most promising candidates. The experiments carried out in the laboratory under gentle vortex extraction conditions (600 rpm, 10 min) showed that citral provided the best extraction efficiencies, with values ranging between 95 and 100% for all sulfonamides.

The obtained results confirm the great potential of hydrophobic monoterpenoids as sustainable and environmentally friendly extractants of sulfonamides (although their polar nature) from aqueous matrices. Besides, the accomplishment of the COSMO-RS theory for the development of guided extraction methods is demonstrated.

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P16

BIOACUMULATION AND DEPURATION OF THREE COMMON ANTIBIOTICS IN BENTHIC ORGANISMS: SEA CUCUMBER, SNAKELOCKS ANEMONE AND BEADLET ANEMONE

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Antibiotics are widely used drugs in human and veterinary medicine, which has attracted great attention in relation to the development of bacterial resistance, currently a problem of great concern for governments and states, as it is related to the resurgence of infectious diseases already eradicated [1]. This concern has motivated the European Union to develop regulations on the protection of marine ecosystems. Decision 2020/1161/EC includes some antibiotics such as ciprofloxacin (CIP), sulfamethoxazole (SMX) and trimethoprim (TMP) in the list of emerging substances to be monitored in the aquatic environment [2]. Understanding the bioaccumulation of antibiotics in aquatic organisms is an important key to understanding their risk assessment [3]. The uptake and elimination of CIP, SMX and TMP were investigated in sea cucumbers (*Holothuria tubulosa*), snakelock anemones (*Anemonia sulcata*) and beadlet anemones (*Actinia equina*) under controlled laboratory conditions. The results show that antibiotics have a particular trend over time during all periods of absorption and depuration. The tissue distribution of antibiotics in sea cucumber is strongly influenced by the structure of the compounds, while CIP is concentrated in the body wall; TMP is concentrated in the digestive tract. Two different approaches were used to estimate bioconcentration factors (BCFs) in different animal models, based on toxicokinetic data and measured steady-state concentrations. The BCF ranges were 456-2731 L/kg, 6-511 L/kg and 9-100 L/kg for TMP, CIP and SMX, respectively. The estimated BCF values obtained classify TMP as cumulative in *A. equina* and *H. tubulosa*, underlining the potential bioconcentration in these marine organisms. A correlation was observed between the BCFs of the target antibiotics and the octanol-water distribution coefficient (D_{ow}) (r^2>0.7). The animal-specific BCF followed the order of beadlet anemone > sea cucumber > snakelock anemone.

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P17

ANALYTICAL METHOD FOR THE ACCURATE DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN BLACK TATTOO INK

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Although the history of tattoos goes back thousands of years, in recent years, the tattoo sector has experienced great growth, becoming more widespread due to the importance of appearance in developed societies. It is estimated that in Spain about 40% of the population has at least one tattoo, and 36% of those have tattoos occupying more than 900 $cm^2$of skin. However, despite the high prevalence of tattoos in the population, the chemical composition of tattoo inks, its pharmacokinetics and their potential health effects are largely unknown [1].

Black colour ink is the most used one in tattoos. The manufacturing of this inks usually involves the thermal combustion of organic matter and therefore polycyclic aromatic hydrocarbons (PAHs) can be generated. Benzo(a)pyrene (B(a)P) is the PAH of most concern due to its toxicity and considered by the International Agency for Research on Cancer (IARC) as carcinogenic to humans (Group 1). Human exposure to B[a]P has also been correlated to cardiovascular and pulmonary diseases [2]. In the regulatory framework, the REACH Regulation [entry 75 of Annex XVII (Regulation (EC) No 1907/2006)], applies to substances in tattoo inks and permanent make-up at European level since 14 December 2020. This regulation restricts the use of substances with known and suspected adverse health effects, setting a maximum concentration of 5 ng/g of B[a]P in tattoo ink.

Despite this context, there are currently no official or national standardized methods for the determination of PAHs in tattoo ink or permanent make-up samples and the methods used in the PAHs determination of textiles or polymers are often employed.

The aim of this study is to develop and evaluate a simple and fast procedure based on ultrasound assisted extraction (UAE) and GC-MS/MS for the determination of 18 PAHs, including Benzo[a]pyrene (B[a]P), in a very complex matrix, such as black tattoo ink. After optimisation, the proposed method allowed the accurate determination of all target compounds. Repeatability (n=4) of the complete UAE plus GC–MS/MS method for the analysis of the endogenous PAHs were in the range 3−15%, whereas reproducibility (n=6), were between 4% and 23%. Finally, the method was applied to samples of commercial black tattoo inks authorised and used in the European Union. The results showed the presence of PAHs in all the samples and therefore, having robust methods for the determination of these organic contaminants in tattoo ink is highly needed.

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P18

STRATEGIES AND ROUTINE ANALYSIS OF PFASs BY UHPLC TANDEM MASS SPECTROMETRY UHPLC-MS/MS *DURING DROUGHT PERIODS*

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Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are a large group of compounds chemically synthesized. Their chemical structure consists of a hydrophobic alkyl chain of variable length completely or partially fluorinated, with a hydrophilic end group. Their chemical properties make them widely distributed across different environmental compartments and more specifically in waters. Many industrial applications are involved in the use of these compounds such as fireproof products, clothing, pans, pharmaceuticals, pesticides,...Some of them can cause adverse health effects and are considered persistent in the environment and can be bio accumulated in different organisms including the human body.

In this work, an accredited analytical methodology based on ISO 17025, has been used for the determination of 31 PFASs in different types of waters as a routine control. According to the European Directive (UE 2020/2184) and RD 3/2023 (Spain) legislation on the quality of water intended for human consumption, a permitted level of concentration of 0,1µg/L has been established as the sum of 20 PFASs. Sampling methodology of PFASs and sample analytical treatment process were improved according to tests studies performed in our laboratory. During drought periods that occurred in 2023-2024, analysis of PFASs in river water, reclaimed water and groundwater, were intensified. In 2023-2024 one year sampling study was performed in order to evaluate the effect of using reclaimed water to recharge the aquifer of Llobregat River. Results showed that 8 of the 31 analyzed PFASs have been detected at levels of concentration higher than their limit of quantification (5-15 µg/L). Concentrations between 0,004 µg/L (PFHpA) and 0.016 µg/L (6:2 FTS) were found in surface water, between 0,004 µg/L (PFHxS and PFHpA) and 0,053 µg/L (6:2 FTS) in reclaimed water and between 0,004 µg/L (PFHxS and PFHpA) to 0,035 µg/L (6:2 FTS) in surface water intake Drinking Water Treatment Plant (DWTP). On the other hand, a higher diversity of concentrations were found in groundwater depending on the origin, although it seems that PFDA, L-PFBS, PFOA, PFHxS and PFBA are the compounds with the highest concentrations (0,010 to 0,058 µg/L). Moreover, this methodology was also applied to perform a study on the efficiency removal of PFASs along a DWTP. Results showed that advanced treatment water, that consists of ultrafiltration followed by reverse osmosis, has a 100% of removal efficiency of PFASs, meanwhile the conventional treatment, ozonation followed by granulated active carbon filtration, between 22% and 62%. In general terms, all the samples analyzed at the outlet of the DWTP revealed values below the limit of quantification of this methodology.

P19

DEVELOPMENT OF AN ANALYTICAL METHOD OF PBDD/Fs IN EMISSIONS SAMPLES

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Over the last decades, bromine has broken into society's eco-cycle through the widespread consumption of brominated flame retardants (BFRs), initially designed to decrease the flammability of several consumer products. Over time, these organobromine compounds and their precursors have become the main sources of polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) in thermal processes [1].

PBDD/Fs are persistent organic pollutants with similar properties to their chlorinated counterparts (PCDD/Fs), sharing an equivalent structure and potentially analogous health effects. However, PBDD/Fs exhibit notable chemical differences, such as the larger bromine atom size, weaker carbon-bromine bond strength, and greater sensitivity to UV degradation [2]. These differences imply that the current standard methods for determining PCDD/Fs in emissions -specially for the sample preparation and instrumental analysis stages- might not be suitable and directly transferable to their brominated analogues. Therefore, modifications or new approaches would be required, as no standardised analytical procedure for PBDD/Fs in emissions samples currently exists [3].

The present research focuses on developing a methodology to analyse PBDD/Fs in emissions. Special emphasis was placed on the instrumental analysis area. In particular, multiple chromatographic variables were closely evaluated to determine the factors that might affect the correct separation and detection of the multiple brominated congeners. Moreover, the sample preparation phase, including extraction, clean-up and fractionation steps, was also studied. In this case, several parameters, such as solvent type, solvent volume, or extraction times, were thoroughly examined within each step, to develop a methodology with optimised analytical performance. The findings will provide a reliable and advanced analytical procedure for PBDD/Fs, addressing a considerable gap in current environmental analysis methodologies.

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P20

DEVELOPMENT OF ANALYTICAL TECHNIQUES FOR MONITORING PFAS IN AQUATIC ENVIRONMENTS

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Per- and polyfluoroalkyl substances (PFAS) comprise a heterogeneous group of molecules with diverse functionalities and sizes. Due to their unique physicochemical properties, PFAS have been extensively utilised in commercial and industrial applications for over six decades. Nevertheless, in recent years, several PFAS have been identified as pervasive environmental contaminants. Perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) are commonly found in various environmental compartments and organisms. Due to their high persistence, toxicity, bioaccumulative potential, and global distribution, some PFCAs and PFSAs are priority substances for ecotoxicological research and regulation. PFCAs and PFSAs resist typical environmental degradation, being less volatile and more water-soluble than legacy persistent organic pollutants (POPs). Aquatic environments serve as their primary reservoirs. Monitoring these substances in global aqueous matrices is essential to understand their impact on marine ecosystems. The analytical determination of PFAS typically involves solid-phase extraction (SPE) followed by high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS).

The objective of this study was to develop and validate an extraction and analysis method for the determination of 22 PFAS (including 11 types of PFCAs, 3 types of PFSAs, 3 types of fluorotelomer sulfonic acids (FTSAs), 2 types of perfluoroalkane sulfonamidoethanols (FASEs), 2 types of perfluoroalkane sulfonamides (FASAs), and one perfluoroalkyl ether carboxylic acid (PFECA)) by high-performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS). The instrumental method was optimised regarding different mobile phase compositions, gradient percentages, flow rates, and injection volumes. Additionally, the ion source parameters and MS/MS parameters were optimised. For the extraction process, the solvent composition was optimised by testing three different types of cartridges. This aimed to understand the complex interactions involved in the sorption of different PFAS families. Various sorbents for extraction, different solvents for elution, sample pH, spinning of the extraction cartridge, salinised vials, glass vials, and plastic vials were evaluated.

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P21

METHOD DEVELOPMENT TO THE DETERMINATION OF GADOLINIUM CONTRAST AGENTS IN PEAT SAMPLES

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Gadolinium-based contrast agents (GBCAs) are compounds commonly used in magnetic

resonance imaging (MRI) to enhance the sharpness of the images obtained [1]. After their administration, the compounds are excreted and finally reach wastewater treatment plants, where they are not removed, and are eventually released into the environment [2]. As part of the research for the reuse of regenerated wastewater, an analytical method, based on the LC(IC)-ICP-MS coupling, was developed for the determination of selected GBCAs in peat. The GBCAs involved in the research were Gadoteridol, Gadobutrol and Dotarem, those widely used in Castellon province health system.

Chromatographic separation was performed on a Hamilton PRP X110 anion exchange column. Due to the presence of Gd(III) in peat samples and its chromatographic behavior similar to Dotarem, a detailed study of the separation was performed. The finally optimized mobile phase consisted of 40 mM EDTA, 30 mM NH_4NO_3 at pH 9.8, and a step gradient of 2,5 % of MeOH. In these optimized conditions, the analytes were separated in less than eight minutes.

Peat samples taken from an experimental greenhouse plant were used to develop the extraction procedure. To this end samples were fortified at 2 levels of concentrations: 10 ng g $^{-1}$ and 50 ng g $^{-1}$. Proper aqueous solutions of standards were added to peat (ensuring the spread of wet through the solid) and left to dry for 48 hours. Then, 2 g of homogenized sample were mixed with 30 mL of KOH 0,5 M and shaken for 30 minutes. Finally, a tenfold dilution step with mobile phase was conducted before instrumental measurement.

The trueness of the method was checked by recovery calculation. To assess repeatability, the whole extraction and measurement procedures was conducted in quintuplicate on the same day (n = 5). Three additional measurements (in duplicate) were performed in three consecutive days to test interday reproducibility.

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P22

PHARMACEUTICALLY ACTIVE COMPOUNDS (PhACs) IN WASTEWATER TREATMENT PLANTS

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After consumption of medications, pharmaceutically active compounds (PhACs) are excreted in the feces and urine and travel in the wastewater to the wastewater treatment plants (WWTPs). However, due to the lack of efficient removal technologies, the effluents released into the aquatic environment could still contain part of these substances. Thus, there are substantial knowledge gaps regarding the effectiveness of removal, the influence on surface water contamination, and the potential transfer of pollutants to the sewage sludge line. To address these issues, the present study investigates the occurrence of 22 PhACs and one metabolite in influents (n=8), effluents (n=8) and sewage sludges before (n=8) and after (n=8) the anaerobic digester collected from two WWTPs located in the Tagus River watershed during 2022.

Water samples (1 L) were spiked with deuterated internal standards and extracted by solid phase extraction (SPE) using Oasis HLB (500 mg, 6mL) cartridges and MeOH as theelution solvent. Spiked sewage sludge samples were extracted with a Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) procedure. Instrumental analysis was conducted by an ultrahigh performance liquid chromatograph coupled to a Triple Quad™ 3500 MS/MS System (UPLC-TqMS/MS, SCIEX, MA). The validated methods meet performance criteria as indicated in SANTE/2020/12830 and SANTE/12682/2019. Limits of quantifications ranged between 5 to 50 ng/L for water samples and between 1 to 50 ng/g dry weight (d.w.) for sewage sludge.

A total of 19 of the 23 target PhACs were quantified in at least one influent sample with median concentrations up to 19 µg/L (acetaminophen). In effluents, median concentrations ranged between 6.8 ng/L (erythromycin) and 2.8 µg/L (irbesartan). Removal efficiencies revealed significant (>70%) degradation for 17 of the PhACs evaluated, nevertheless excluding atorvastatin, all the compounds quantified in the influent were still present in the WWTP effluents. Interestingly, gemfibrozil was the PhAC with the lowest degradation efficiency (2%). Results corroborate that WWTP effluents are the main source of PhAC pollution in this river ecosystem. Nevertheless, the physicochemical properties of some of these PhACs allow them to bind to the sediment and attenuate their concentration in the water. Additionally, the results confirmed the transfer to the sludge of those PhACs with a greater tendency to bind to organic material (Koc). Clotrimazole and miconazole were two of the major compounds in the two WWTPs quantified in more than 88% of the sludge samples. Unlike in the water line, the treatment applied was not effective in eliminating PhACs from the sludge.

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P23

OCCURRENCE AND TRANSFERENCE OF PHARMACEUTICALLY ACTIVE COMPOUNDS (PhACs) IN SEDIMENTS AND FISH FROM TAGUS RIVER BASIN

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The occurrence of PhACs in river waters is well established. However, little is known about the mobility of these compounds towards other environmental compartments such as sediments or biota. This environmental transfer threatens the survival of the affected species and the quality of the entire river ecosystem. To address this issue, the present study investigated the presence of 22 PhACs and one metabolite in river sediments (n=28) and fish samples (n=24) collected from the Tagus River watershed during 2020, 2021, and 2022.

An adapted QuEChERS extraction method was carried out to analyze the target PhACs in sediments, while for fish samples an organic solvent extraction followed by an SPE cleanup step was performed. Instrumental analysis was conducted by ultrahigh performance liquid chromatography connected to a Triple Quad™ 3500 MS/MS System (UPLC-TqMS/MS, SCIEX, MA) followed by quantification with deuterated standards.

Validation experiments meeting SANTE/2020/12830 and SANTE/11312/2021 criteria were conducted with samples where PhACs were not detected. Limits of quantifications ranged between 1 to 50 ng/g for sediments and between 5 to 50 ng/g dry weight (d.w.) for fish. 12 PhACs were quantified in at least one sediment sample. Antidepressants were the majority compounds in sediments with median concentrations between 24 ng/g and 47 ng/g d.w. and quantification frequencies above 68%. However, PhACs with low water solubility and great affinity to bind to organic matter such as clotrimazole or miconazole were found in more than 57% of the sediment samples. In addition, compounds positively charged at the pH of the medium, such as o-desmethylvenlafaxine, also showed a tendency to bind to the sediments, while negatively charged compounds (gemfibrozil, ibuprofen, ketoprofen, naproxen or valsartan) showed the opposite behavior. On the other hand, only two PhACs were found above LOQ in fish samples. Clotrimazole obtained the highest frequency of quantification since it is the compound with the greatest tendency to bioaccumulate (BCF=6297) of those studied. No temporal tendencies ($p>0.05$: Kruskal-Wallis test) were found. According to results obtained in surface water sampled in the same period, areas with the highest ∑PhACs concentration in river water showed the highest PhAC levels in sediments and biota, revealing a possible mobility between these environmental compartments. To evaluate the environmental impact of these compounds on the aquatic ecosystem, risk quotient ratios (RQs) were calculated. The RQs obtained in sediments were all below 0.01 at central (P50) and the worst (P95) scenarios, so under the evaluated conditions the risk to aquatic organisms is negligible.

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IDENTIFICATION OF MOLECULAR BIOMARKERS LINKED TO HYDROPHOBICITY OF CROPS USING HIGH-RESOLUTION MASS SPECTROMETRY

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The hydrophobicity of crop surfaces is crucial for plant physiology and environmental interactions, significantly influencing water retention, pathogen resistance, and overall plant health. This characteristic affects how water droplets behave on leaf surfaces, impacting transpiration, nutrient uptake, and photosynthesis efficiency. High hydrophobicity enables plants to shed excess water quickly, reducing the risk of fungal infections and other pathogens that thrive in moist conditions. However, it can also impact the ability of plants to retain moisture during dry periods, affecting drought resistance and irrigation efficiency. This study aims to identify molecular biomarkers associated with the hydrophobicity of different crop surfaces using high-resolution mass spectrometry (HRMS). The hydrophobicity level of nine crops was analyzed using the water drop penetration time (WDPT) test. The lipid fraction of each crop type, extracted with a mixture of organic solvents (DCM/MeOH 1:1 v/v), was analyzed using gas chromatography (Agilent Technologies, Sta. Clara, CA, USA; Mod. 8890) coupled to an ultra-high resolution quadrupole time-of-flight mass spectrometer (Q-TOF MS Mod. 7250). PLS regression models with ParLeS software were used to analyse chromatograms and identify biomarkers surrogated to hydrophobicity. Statistical pre-processing included SNV correction, median filter de-noising, and mean centering; model accuracy and complexity were assessed using Root Mean Squared Error (RMSE) and the Akaike's Information Criterion (AIC). Key chromatogram peaks were identified using Variable Importance for Projection (VIP) values, ensuring overfitting was avoided by comparing with models from randomized WDPT data. In addition, an omic approach was applied using various indices, including factor loadings of PLS models, Pearson's R-squared coefficients, and subtraction of average values of compound abundances in groups of samples with significant differences in WDPT values, to identify compounds proxies for hydrophobicity. Our findings reveal specific lipid molecules that strongly correlate with hydrophobicity. These biomarkers offer new insights into the molecular basis of hydrophobicity, providing potential targets for genetic and agronomic strategies to enhance crop resilience and water-use efficiency. This research highlights the importance of molecular-level traits in improving crop performance and adaptation to diverse environmental conditions.

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P25

BIOACCUMULATION AND TRANSFORMATION OF PLASTIC ADDITIVES IN HYDROPONICALLY GROWN PLANTS: IMPLICATIONS FOR SAFE WATER REUSE

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Water scarcity is a critical global issue, exacerbated by climate change and increasing water demand. Reusing water, especially in agricultural irrigation, has become an essential strategy to address this scarcity [1]. However, reclaimed water often contains organic micropollutants, including plastic additives, that originate from widespread plastic pollution and microplastics in the environment. These contaminants can persist through wastewater treatment processes and accumulate in crops, potentially entering the food chain [2]. Thus, it is essential to assess and mitigate these risks to ensure the safe use of reclaimed water in agriculture and protect public health. This study explores the uptake and bioaccumulation of specific plastic additives and the formation of their transformation products (TPs) in a hydroponic system. The research focuses on Carex (Carex praegracilis) for phytoremediation and lettuce (Lactuca sativa) for crop production. The irrigation water was spiked with seven plastic additives commonly associated with textiles, packaging, and tire wear particles: benzotriazole-1H (BTR), bisphenol S (BPS), 1,3dio-tolylguanidine (DTG), hexamethoxymethylmelamine (HMMM), benzothiazole (BTZ), tris(2chloroethyl) phosphate (TCEP), and benzophenone-3 (BzP). Ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) was employed for targeted analysis of these additives in both water and plants to assess their uptake and bioaccumulation. Additionally, liquid chromatography-high-resolution mass spectrometry (LCHRMS) was used for suspect screening to identify TPs. The goal of this research is to improve our understanding of the behaviour of plastic additives in water reclamation scenarios, thereby contributing to effective phytoremediation techniques and safer agricultural practices.

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CHIRAL DETERMINATION OF AMPHETAMINE-TYPE SUBSTANCES IN ENVIRONMENTAL WATERS BY SOLID PHASE EXTRACTION FOLLOWED BY CAPILLARY ELECTROPHORESIS-TANDEM MASS SPECTROMETRY

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The determination of drugs of abuse has been gaining increasing attention among the scientific community as drug consumption is considered a major global public health issue. Amphetamine-type compounds are among the most widely consumed drugs worldwide [1]. Due to their consumption, these compounds can be found in various environmental waters. In the present study, river water, as well as influent and effluent waters from wastewater treatment plants (WWTP) were studied. Amphetamines present a chiral center with two different enantiomers that have different pharmacokinetic and pharmacological properties. Therefore, it is important to develop methods to distinguish between these enantiomers [2]. An effective and straightforward strategy to achieve chiral separation is the use of capillary electrophoresis (CE), by simply adding a chiral selector to the background electrolyte (BGE). To overcome the limited sensitivity typically inherent to CE when coupled with UV detection, in this study, CE was coupled with a tandem mass spectrometry detector (MS/MS), and this influenced the selection of the chiral selector [3], and for that purpose, some different cyclodextrins were evaluated as chiral selectors. The optimal conditions were determined to be the addition of 0.1% of 2-Hydroxypropyl-β-cyclodextrin and 0.1% of γ-cyclodextrin to the BGE, as the chiral selector.

Due to the complexity of the environmental water matrices and the lower concentration at amphetamines could be found in these matrices (in the µg/L range), a pre-treatment strategy was required. Solid phase extraction was the pre-treatment technique selected, specifically, using a mixed-mode cation exchange sorbent, ExtraBond SCX. Using 100 mL of influent WWTP water and 250 mL of river and effluent WWTP water of sample and 5 mL of 5% of NH_4OH in methanol as the elution solvent, recoveries ranged between 40 and 67% for all amphetamines studied, in the different environmental waters. The limits of detection were range from 0.1 to 0.8 µg/L. Samples from the Ebre river and from WWTP of Reus and Tarragona (Catalonia, Spain) were analyzed, confirming the presence of some of the compounds in some WWTP water samples, being both enantiomers of MDMA detected in effluent and influent waters, where. Additionally, R-Amphetamine could be quantified in some influent WWTP waters. Conversely, the studied compounds could not be detected in river water.

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P27

PER- AND POLY-FLUOROALKYL SUBSTANCES (PFAS) IN FOLLICULAR FLUID FROM WOMEN UNDERGOING *IN VITRO* FERTILIZATION (IVF) DURING OOCYTE RETRIEVAL PROCEDURE

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PFAS are chemicals widely detected in human matrices and associated with potential adverse reproductive health effects [1]. Concerns about female reproductive toxicity due to PFAS are growing, but their impact on human preconception exposure is sparse [2]. Experimental studies have shown that PFOS impairs oocyte maturation and viability in pigs [3]. Additionally, PFOA exposure may alter the metabolic composition of follicular fluid (FF), impacting the ovarian reserve function [4]. This study aimed to evaluate PFAS in FF from 20 healthy, fertile women undergoing IVF during the oocyte retrieval procedure (male factors of infertility). Clinical data collected included age, body mass index (BMI), anti-Mullerian hormone (AMH) in serum, glucose in FF, and retrieved cumulus-oocyte complex (COC). Fifteen out of 19 targeted PFAS were detected in FF samples. PFOS, Br-PFOS, PFHxS, PFOA, PFNA, PFDA, and PFUnDA were found in all samples, while PFHpA and FOSA were above detection limits in 90% and 80% of samples, respectively. The remaining ones were barely detected in less than 30% of samples. Total PFAS concentration ranged from 1.02 to 4.89 ng/mL (mean 2.57 ng/mL). The PFAS profile was dominated by PFOS (46.7%), followed by PFOA (17.0%) and PFHxS (11.2%). PFAS profiles and concentrations were similar to those detected in FF in females from China and Australia [1, 2]. In the score plot of different PFAS compounds, PC1 accounted for 48.5% of the data variation, indicating the most detected PFAS compounds, while PC2 explained an additional 15.8%, separating PFCAs and PFSAs. PCA analysis showed PFCAs dispersed along the positive direction of PC2, while PFSAs dispersed along the negative direction. Clinical data scattered similarly with PFSAs, especially AMH, which correlated positively with PFOS, Br-PFOS, and PFHxS. PFHpA correlated negatively with AMH and COC. Interestingly, PFAS have been found before inversely associated with AMH concentrations in nulliparous women and positively in parous participants [5]. Conversely, a different study suggested no association between in-utero PFAS exposure and AMH levels in female adolescents [6], nor with BMI and age [7]. In conclusion, further large-scale studies are needed to investigate the relationship between PFAS levels and female reproductive health.

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FLOW-MODULATION COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY FOR NON-TARGET ANALYSIS OF ORGANIC POLLUTANTS IN ENVIRONMENTAL SAMPLES

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Water pollution continues to be a major health and ecological problem that influences the quality of life and the environment. The increased release into the water bodies of a large amount of dangerous and toxic substances, resulting from human and industrial activities, cause adverse effects on humans and living organisms. Over the years, regulatory efforts have been underway to reduce or limit their use and production, launching monitoring programs for the detection of priority and emerging pollutants. However, a large number of contaminants are still unknown and their analysis remains a challenge, especially for water samples. Comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC–TOFMS) has proven to be more useful for the analysis of volatile and semi-volatile compounds in complex samples than conventional one-dimensional GC since it provides greater separation capacity and unique structured chromatograms.
In the present work, the feasibility of a new flow-modulation comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GCxGC-TOFMS) method for non-target screening of organic contaminants in aquatic environments is evaluated. GCxGC separation was carried out using a GC column combination of Rxi-5 SilMS x Rxi-17 SilMS and a new flow modulator (Flux^{TM} – LECO Corp.). Operating parameters of the flow modulator, such as injection/divert steps and the modulation time, were optimized to achieve maximum peak capacity. The detection and identification of the suspect and non-target compounds were accomplished using a TOFMS (Leco Pegasus BT 4D TOFMS) operating in electron ionization and full-scan mode (*m/z* 45-650). In addition, criteria were established for the identification and structural confirmation of non-target compounds using the chromatographic information (^{1}D and ^{2}D retention times), mass spectral data (similarity to the NIST and in-house libraries, fragmentation pattern, isotopic distribution), and information available in public databases. The developed method was applied to the analysis of surface water and effluents of wastewater treatment plants, allowing the (tentative) identification of more than 300 semi-volatile contaminants per sample, most of them considered emerging contaminants. The main detected pollutant groups included pharmaceuticals, flame-retardants, personal care products, linear and aromatic hydrocarbons, byproducts, and metabolites, among others. The results and conclusions of this research are presented here.

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HIGH RESOLUTION ANALYSIS OF BIOGENIC VOLATILE ORGANIC COMPOUNDS (BVOCs) EMITTED BY INTACT TOMATO PLANTS USING SPE/GC-TOF-MS

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Biogenic volatile organic compounds (BVOCs) are secondary metabolites released by plants that mediate important ecological processes, including interactions between plants and their pollinators, herbivores, herbivores' predators and parasitoids, and even other plants in the surroundings [1]. BVOCs are differentially produced according both to environmental factors that affect plant development and to biotic stress affecting the plant [2]. Structurally, BVOCs belong to the group of terpenoids, aromatic compounds and certain alkanes, alkenes, alcohols, esters, aldehydes, and ketones [3]. While the chemical structures of BVOCs are not typically complex, the naturally produced blends are, and changes in their proportion may impact its ecological function [3]. Even though tomato is the second most cultivated vegetable in the world [4], the studies of BVOCs emitted by intact plants are scarce. Therefore, we reported for the first time the BVOCs emitted by actively growing tomato plants using high resolution GC-TOF-MS. Potted tomato plants (var. San Pedro) (n=9) were grown at room temperature for 30 days enclosed in 17 L teflon-sealed glass cylinders. A continuous stream of charcoal-filtered air (2 L min^{-1}) was pushed through the system and BVOCs were adsorbed on glass cartages filled with 50 mg HayeSep® Q (Hayes Separations, Inc., Bandera, TX, USA). The compounds were eluted with 1 mL of double-distilled n-hexane, n-tridecane (24 µg) added as internal standard (IS) and the solution concentrated to 100 µL under a N_2 stream. Samples were then analyzed using a GC (Agilent Technologies, Sta. Clara, CA, USA; Mod. 8890) coupled to an ultra-high resolution quadrupole time-of-flight mass spectrometry (Q-TOF MS Mod. 7250). Masses were acquired in the range of 50-600 u with an accuracy < 1 ppm according to the instrument's autotune reports performed before each sample run. A total of one 131 compounds were quantified, with hydrocarbons and monoterpenes being the most abundant and β-pinene remarkably the most abundant structure. Up to 100 compounds were identified comparing retention indexes, mass spectra with libraries available and their exact masses when identified of these, 63 BVOC's are reported here for the first time in tomato.

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P30

GAS CHROMATOGRAPHY - TANDEM MASS SPECTROMETRY METHOD FOR THE DETERMINATION OF SELECTED ENDOCRINE DISRUPTORS IN HUMAN FAECES

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Endocrine disrupting chemicals (EDCs) are environmental pollutants that can enter our bodies modifying proper functioning of the endocrine system and causing diverse pathologies. Among the toxic effects, problems related to both female and male reproduction (e.g. endometriosis, breast and prostate cancer or reduced semen quality) and obesity (e.g. type II diabetes mellitus) have been demonstrated [1]. Gut microbiota is related to metabolism and obesity. EDCs have also been shown to potentially play a role in these processes [2]. In this context, faeces are a convenient matrix that is useful for identifying the quantity of EDCs that reach the intestine and the extent to which the organism is exposed to these pollutants. The present work developed a new CG-MS/MS analytical method to determine 17 compounds belonging to the paraben and bisphenol families found in human faeces. The extraction method was optimized using an ultrasound-assisted extraction technique followed by a clean-up step based on QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) technique. Optimization was performed using design of experiments. In validation analysis, the method was proven to be linear in a wide range. R-squared outcomes were between 95 and 99%. Selectiveness and sensitivity outcomes were acceptable, with detection limits being between 1 and 10 ng g^{-1} in all cases, whilst quantification limits were between 3 and 25 ng g^{-1} in all instances, with the except of bisphenol AF. The method was deemed accurate, with recovery values being close to 100% and relative standard deviations being lower than 15% in all cases. Applicability was examined by analysing 13 samples collected from volunteers (male and female). All samples were contaminated with at least one of the analytes studied. The most commonly found compounds were methylparaben and bisphenol A, which were detected in almost all samples and quantitatively determined in 11 and 12 samples, respectively. Of the 17 compounds analysed, 11 were found in at least one sample. Outcomes demonstrate that faeces can be a good matrix for the determination of exposure to contaminants of interest here.

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DETERMINATION OF OBESOGENS IN BIOLOGICAL SAMPLES AND THEIR RELATIONSHIP TO CHILDHOOD OVERWEIGHT/OBESITY

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Endocrine disruptors (EDs) are hormonally active substances that alter the normal balance of the endocrine system and energy metabolism, contributing to the development of overweight/obesity (1). EDs include bisphenols, which are widely used in the production of food contact plastics, with the oral route via the diet being the main route of exposure (2). Hair and nails are considered good biomarkers of contamination for prolonged exposure. In contrast, urine reflects short-term exposure and may vary throughout the day. The present study focused on the determination of bisphenols in hair, nails and urine samples of schoolchildren and their relationship with the incidence of childhood overweight/obesity. A total of 124 cases and 179 controls aged 6-12 years from the province of Granada were recruited. The analysis of compounds was carried out using UHPLC-MS/MS. In addition, binary logistic regression was performed to analyse the influence of the presence of bisphenols on overweight/obesity in the study population. The main bisphenols detected in the biological matrices were bisphenol A (BPA), bisphenol AF, bisphenol F (BPF), bisphenol S and bisphenol AP in decreasing order. In the case of total bisphenols determined in nails, the highest concentrations were found in schoolchildren with the highest body mass index (BMI). However, in urine and hair they were found in schoolchildren with a lower BMI. The results suggest that bisphenol F in nails was positively associated with overweight/obesity in children (OR= 4.87; p= 0.020). For the other matrices and bisphenols studied, no statistically significant associations were found. This work is the first to report the association between BPA and 11 analogues analysed in three biological matrices and childhood overweight/obesity. The findings suggest that higher detected concentrations of BPA in nails are associated with a higher likelihood of being overweight/obese in schoolchildren. However, further epidemiological and toxicological studies are needed to clarify the role of bisphenols on weight gain.

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THERAPEUTIC MONOCLONAL ANTIBODIES ANALYZED BY CAPILLARY ELECTROPHORESIS WITH SDS

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Monoclonal antibodies (mAbs) are proteins that belong to the immunoglobulins G (IgG) group and they provide more specific and personalized therapeutic alternatives in various diseases. Currently mAb therapy is one of the fastest-growing areas within the pharmaceutical industry. Aggregation is a frequent mAb degradation pathway [1]. Size variants, formed during production and storage, are considered as one of most important critical quality attributes (CQA) since high concentrations of them can generate toxicity or adverse effects. Strict controls are required to guarantee the quality of these therapeutic drugs. Therefore, developing analysis methods that allow mAb size variants related to fragment and aggregates to be revealed are necessary. Capillary electrophoresis with sodium dodecyl sulfate (CE-SDS) allows analytes to be separated based on their molecular size.

In this work, the usefulness of CE-SDS using capillaries and buffer-gel prepared in the laboratory to analyze different commercial therapeutic mAbs has been studied. Drugs based on mAbs of IgG1 (bevacizumab, ocrelizumab, guselkumab, infliximab and ustekinumab) and IgG4 (natalizumab, and reslizumab) subclasses have been analyzed. In addition to the reference drugs, some of their biosimilars have been also studied. Besides, the developed CE-SDS methods have also been used to evaluate degraded and stressed samples.

CE-SDS analyses under reducing and non-reducing conditions have allowed us to observe peaks that, due to their migration times, are tentatively assigned to different fragments and/or aggregates of the mAbs. No notable differences have been observed in the CE profiles of reference drugs *versus* their biosimilars. Aging of the Ocrevus® (ocrelizumab) drug sample prepared with SDS and mercaptoethanol modifies the heavy chain (HC)/light chain (LC) ratio and results in the presence of peaks with a molecular size larger than the HC. For this sample, as the proportion of HC decreases, more peaks of high molecular size, possibly HL combinations or aggregates, emerge. In the expired and temperature-stressed Avastin® (bevacizumab) samples, fragments and high molecular size species that were not seen in the valid sample have been distinguished.

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RISK ASSESSMENT IN ANALYTICAL METHOD DEVELOPMENT PROCEDURE ACCORDING TO ICH Q14 GUIDELINE. APPLICATION EXAMPLE

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The ICH Q14 guideline3, along with the ICH Q92 and ICH Q21 guidelines, provides a comprehensive framework for the quality and evaluation of analytical methods in the pharmaceutical industry. ICH Q14 focuses on the development of analytical methods, establishing a lifecycle approach. It encourages a deep understanding of the method from its inception to implementation, emphasizing the need to consider variability and robustness from early stages. It promotes a systematic and scientific approach, considering risk management and proper documentation to ensure the quality of the analytical method. ICH Q2 addresses the validation of analytical methods, describing acceptance criteria and essential parameters such as precision, accuracy, specificity, and robustness. Validation is a key component in the analytical method lifecycle described in ICH Q14, ensuring that the developed method meets required standards and can reliably reproduce results. ICH Q9 provides a framework for quality risk management in pharmaceutical development and manufacturing. It offers principles and tools to identify, evaluate, and control risks throughout the product lifecycle. Integrated with ICH Q14, risk management helps identify critical areas in the development of the analytical method, allowing efforts to be prioritized based on their potential impact on product quality. The integration of the ICH Q14, ICH Q2, and ICH Q9 guidelines ensures a holistic and rigorous approach in the development, validation and risk management of analytical methods, enhancing the quality and safety of pharmaceutical products4. The systematization of analytical method development, along with the knowledge gained from risk assessment, provides clear advantages in both the time required for development and the establishment of operational controls that enable the prevention and detection of errors in routine use. This communication presents an example of the application of the integration of these guidelines, demonstrating the advantages this approach brings to the development and reliability of analytical methods.

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DETERMINATION OF OBESOGENS IN FOOD AND THEIR RELATIONSHIP TO CHILDHOOD OVERWEIGHT/OBESITY

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A growing number of studies associate increased overweight/obesity with exposure to certain environmental chemical pollutants (1). Findings to date found that these compounds promote inadequate fat storage by interfering with adipogenesis (2). Since exposure to obesogens early in life has stronger and more pronounced effects at lower doses, it is important to study their possible effects in childhood (3). The purpose of this research was to determine the presence of bisphenols in foods and to assess the relationship between dietary exposure and the development of overweight/obesity in a Spanish child population. Dietary and anthropometric data were obtained from 303 schoolchildren. A total of 98 food samples were analysed for the presence of bisphenol A (BPA) and its analogues. Sample treatment was based on QuEChERs and UHPLC-MS/MS was the analytical technique selected for analyte determination. Using a food frequency questionnaire, dietary exposure to bisphenols was assessed through the foods analysed. Finally, logistic regression was used to analyse the influence of dietary exposure on overweight/obesity. BPA was detected in most of the samples analysed (range 1 to 409 ng g^{-1}), followed by BPS (range 5 to 39 ng g^{-1}). Regarding the relationship between bisphenol exposure and overweight/obesity, an increased likelihood of overweight and obesity was observed in girls exposed to high levels of BPA from meat and eggs (OR: 2.70; p= 0.050), although no consistent associations were observed in boys and the rest of bisphenols. According to the findings, BPA affect the development of overweight/obesity in girls. However, its exact impact remains unclear and therefore longitudinal studies are needed to definitively clarify the association between bisphenols exposure and childhood overweight/obesity.

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P35

EXPLORING CO-EXPOSURE OF MYCOTOXINS AND PESTICIDES THROUGH HUMAN BIOMONITORING: EFFECTS OF CONVENTIONAL AND ORGANIC DIETS

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Pesticides and mycotoxins are commonly found in plant-based foods, contributing to their presence in the human body as evidenced by biomonitoring programs. However, there is limited knowledge about their co-occurrence patterns. While intervention studies have demonstrated that organic diets can significantly reduce pesticide levels, their impact on mycotoxin exposure has been overlooked. This study pursued two objectives: (i) to characterize the simultaneous presence of mycotoxins and pesticides in human urine samples using biomarkers of exposure; and (ii) to investigate the influence of organic foods on these co-exposure patterns. This pilot study involved 20 healthy volunteers consuming either exclusively organic or conventional foods during a 24-h diet intervention. Their first-morning urine samples were collected, minimally treated, and analyzed using LC-Q-ToF-MS by means of a multitargeted method to detect the presence of selected pesticides and mycotoxins.

Among the 52 screened compounds, four mycotoxins and seven pesticides were detected in over 25% of the samples. Deoxynivalenol (DON) and the non-specific pesticide metabolite diethylphosphate (DEP) exhibited the highest frequency rates (100%) and the highest median concentration levels among detected pesticide biomarkers (18.7 µg/g creatinine creatinine-adjusted or 23 µg/mL non-adjusted creatinine). Correlations were observed between urine levels of mycotoxins (DON, ochratoxin alpha [OTα], and enniatin B [ENNB]) and organophosphate pesticide metabolites DEP and 2-diethylamino-6-methyl-4-pyrimidinol (DEAMPY). The study suggested a reduction in ENNB and OTα levels and an increase in β-zearalenol levels in urine after a short-term replacement with organic food. However, due to the reduced sample size and short duration of the study, more research is needed to fully understand the human exposome and to refine chemical risk assessment.

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CHROMATOGRAPHIC ANALYSIS OF THE IMPACT OF ORGANIC AMENDMENTS ON THE COMPOSITION OF SOIL AND FRUIT IN SUPERINTENSIVE OLIVE ORCHARDS

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The intensification of agricultural production is essential to address the global challenge of food shortages due to increasing world population, which together with the problem of the lack of management of agricultural residues have sparked an interest in the application of organic waste materials as soil amendments [1].

This study investigates the impact of three different organic amendments on the composition of an alkaline soil and olive fruits of superintensive olive orchards. The amendments included olive pruning biochar (B), commercial green compost (CP), and a combination of biochar and compost (B+CP). Prior to amendment, both the soil and the amendments were thoroughly characterized. One of the indicators of olive quality is its lipid content and composition [2]. Thus, over a period of two years' post-amendment, the study evaluated their effects on the quality and production rates of olive fruits.

Lipids were extracted using *n*-hexane from both the soil and the harvested olives, and subsequently analyzed using gas chromatography-mass spectrometry (GC-MS). The findings indicate a significant stratification in lipid composition within the soil: higher alkane percentages were noted in the deeper soil layers across most treatments, whereas sterols predominated in the surface layers. Soils amended with compost alone exhibited the lowest fatty acid content.

Regarding the olives, those from trees treated with biochar showed increased nitrogen compound levels compared to other treatments. In contrast, olives from unamended, rainfed soils demonstrated a greater concentration of aromatic compounds. Fatty acid content was lowest in olives from both un-amended soils and those receiving compost. These results highlight the nuanced influences of different organic amendments on both soil and fruit composition in super intensive olive cultivation, suggesting pathways for optimizing agricultural outputs through tailored amendment practices.

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SIMULTANEOUS DETERMINATION OF PESTICIDES AND MYCOTOXINS IN FISH FEED BY UHPLC-HRMS

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Intensive aquaculture is a growing practice to meet the high demand of food. However, due to this high demand, novel non-marine ingredients are being incorporated into feed formulations. In this matter, contaminants that are not typically found in the marine environment could enter the food chain. Mycotoxins and pesticides are compound frequently detected in these alternative ingredients, with mycotoxins also potentially emerging during storage. To address this, maximum residue levels for pesticides and some mycotoxins have been set by European Commission in feed samples [1,2]. The objective of this study was to develop a multi-analyte method for the determination of 28 mycotoxins and 11 pesticides in aquaculture feed samples. Various extraction methods were tested, selecting finally a solid-liquid extraction (SLE) with MeCN:H_2O 80:20 (*v/v*) containing 0.1% formic acid (*v/v*), followed by a dispersive solid-phase extraction with $MgSO_4$ and C18 for cleaning up. A Hypersil GOLD aQ column was used for chromatographic separation, and a Q-Exactive Orbitrap, operating in positive and negative ionization modes, was used for compound detection. The method was fully validated according to the parameters established in the SANTE guideline [3]. Limits of detection and quantification ranged from 0.03 to 25 µg/kg and from 0.13 to 50 µg/kg for most compounds, respectively. Trueness was checked by recovery studies, exceedeing 71% for all analytes, except for 3-acetyl deoxynivalenol (3-AcDON) (69%), aflatoxin B1 (AFB1) (65%), α-zearalenol (47%), acetamiprid (ACE) (61%) and cypermethrin (57%), although precision was satisfactory, with RSDs, below 20% in all cases. A total of 36 feed samples with different novel ingredients were analyzed, and the most frequently detected compounds were the pesticides pirimiphos-methyl, carbendazim, tebuconazole and ACE, which come from the agricultural products, and the mycotoxins enniatins B and B1, AFB1, DON, zearalenone and alternariol. None of them exceeded the limits established by the European Union.

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ANALYTICAL METHOD IMPLEMENTATION FOR THE DETERMINATION OF TOTAL AMINO ACIDS IN SAMPLES OF CHICKPEA FLOUR BY HIGH RESOLUTION LIQUID CHROMATOGRAPHY

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Introduction

Chickpea flour, derived from ***Cicer arietinum***, is a valuable source of high-quality plant proteins. This study focuses on evaluating the applicability of an HPLC method to determine its amino acid profile.

Methodology

An analytical method was implemented using high-performance liquid chromatography (HPLC) to identify and quantify the amino acids present in 3 commercial chickpea flour samples. Samples were hydrolyzed under acid conditions and on-line derivatized prior to the injection into the HPLC system. The evaluation of parameters such as linearity and detection limit were determined.

Results and discussion

Linearity was defined within the concentration range of 25-1000 pmol/µL (determination coefficient ($r^2 \geq 0.99$)) because, for some amino acids, the level of 10 pmol/µL did not allow for calibration curves with adequate determination coefficients. This led to the definition of the method's limit of detection (LOD) at 10 pmol/µL, as amino acid peaks were visible at this concentration. The study identified histidine, lysine, and leucine as the most abundant amino acids in chickpea flour samples.

The results demonstrate variability in amino acid content among different chickpea flour brands, highlighting the need to standardize production methods to ensure consistent nutritional quality.

Conclusions

The study validates the use of HPLC-DAD for analyzing amino acid profiles in chickpea flours, providing a useful tool for the food industry and offering a scientific basis for developing more food products.

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GC-MSMS 200+ MULTI-RESIDUE PESTICIDE SCREENING WORKFLOW - COMPARISON OF CONVENTIONAL 30m COLUMN AND LPGC KIT

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Throughput is one of the most important parameters in the lab. While there are numerous ways to increase the speed of analysis, the low-pressure gas chromatography (LPGC) is unique in going towards short, wider bore column rather than short and narrower one. Coupling this type of column with a narrow gurad column with a restrictor allows a normal head pressure at the inlet, while the analytical column is operated under near-vacuum conditions. The low pressure inside the wide-bore column shifts the optimum linear velocity about a factor 7 higher, which allows for faster analysis without a total loss of efficiency. The wider ID and thicker film provide also higher capacity, robustness and inertness. To demonstrate the technique, spinach was spiked with over 200 pesticides at two levels, 100 ppb and 10 ppb and analysis on conventional column (Rxi-5MS column, 30 m x 0.25 mm x 0.25 µm) was compared to the analysis on the LPGC column set.

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LIQUID CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY AS A TOOL FOR THE DESIGN OF A NOVEL SMOOTHIE FORMULATION WITH A HIGHLY DIVERSIFIED (POLY)PHENOLIC PROFILE

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Smoothies are blended beverages made by combining more than one fruit and/or vegetable. Thus, mixed smoothies might provide a sensory appealing and convenient way to promote fruits and vegetables intake as well as their variety, resulting in consumption of a wider range of dietary bioactive compounds, including (poly)phenolic compounds.

A well-designed selection of specific but varied plant-based ingredients might result in novel beverages with a high content and diversified (poly)phenolic compounds and, consequently, enhanced health benefits. Thus, the aim of this work was to propose a strategy, based on LC-MS/MS metabolomics, for the design of new fruit and vegetable-based smoothies with a broad (poly)phenolic spectrum.

To this end, an in-depth and accurate LC-MS/MS method was developed, targeting the characteristic (poly)phenols of potential plant matrices: Granny Smith apple, green celery, green chicory, borage, Swiss chard, and peppermint. To identify (poly)phenols of each plant matrix, a preliminary analysis was carried out in full scan mode, scanning in the mass range (m/z) from 100 to 1000. Subsequently, a selective product ion analysis (MS/MS) was performed to determine the fragmentation pattern of each molecular ion. Finally, an ion multiple reaction monitoring (MRM) mode analysis was employed for quantification. The LC-MS/MS targeted approach included 57 (poly)phenolic compounds providing an extensive coverage for a large variety of structurally different (poly)phenols.

The incorporation of dried green chicory and peppermint leaves into a liquid based composed of Granny Smith apple and green celery was promising for the design of novel smoothies with an enhanced (poly)phenolic profile. The enrichment of a fruit and vegetable-based beverage with leafy green vegetables led to a smoothie containing high amounts of (poly)phenols (2947.68 ± 5.17 µg/g dm) as well as a highly diversified profile characterized by the most representative (poly)phenols of each plant ingredient. A total of forty-three (poly)phenolic compounds belonging to six different families; hydroxycinnamic acids, flavan-3-ols, flavanones, flavonols, flavones and dihydrochalcones, were accurately identified and quantified using pure standards in the smoothie.

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OPTIMIZATION OF A NEW SPME GC-MS METHOD FOR OREGANO AUTHENTICATION

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Oregano has been reported to be the most consumed herb due to its highly appreciated organoleptic properties, and a frequent target of adulteration [1]. The detection of fraudulent practices in oregano, especially difficult when chemotaxonomically similar species such as marjoram are used as adulterants, requires the use of highly efficient and sensitive analytical approaches. Despite their advantages in terms of greenness, speed and affordability, methodologies based on solid-phase microextraction followed by gas chromatography coupled to mass spectrometry (SPME GC-MS) have been scarcely applied for volatile profiling of this aromatic plant [2]. Therefore, the aim of this work was the optimization of a new SPME GC-MS method for the detection of oregano adulterated with marjoram and its application to assess the genuineness of commercial oregano samples.

First, a preliminary optimization of volatile isolation by SPME (10 mg of ground sample placed in a 4-mL vial, Divinylbenzene/Carboxen/Polydimethylsiloxane SPME fibre, etc.) and of chromatographic parameters in GC-MS analysis (HeavyWAX column, injection: 250 °C, split ratio 1:50) was carried out. Then, a 3-level factorial experimental design was used for the optimization of SPME extraction temperature (T_{ext}) and time (t_{ext}). Optimal SPME conditions providing the maximum recovery of oregano volatiles throughout the entire elution range were T_{ext} = 57 °C and t_{ext} = 39 min, for an equilibrium time of 15 min.

The optimized SPME GC-MS method was further applied to the multicomponent characterization of the volatile composition of commercial oregano and marjoram samples, and of oregano intentionally adulterated in the laboratory with 10-60% marjoram. These results (percent data for 61 volatiles of different functionality) were subjected to principal component analysis in order to explore the natural grouping of the samples under study. Clusters corresponding to the different carvacrol:thymol chemotypes were identified. These clusters did not appear to be related to the geographical origin or the cost of oregano samples. Regarding adulterations, positive (*cis*-sabinene hydrate, *cis*-sabinene hydrate acetate, etc) and negative (2-methoxy-p-cymol and carvacrol) markers were identified. As compared to previous literature, an improved level of detection (30% marjoram) was provided by this new methodology. Labeling frauds in some of the *Origanum vulgare* samples were also evidenced by the presence of markers of other *Origanum* species (e.g. borneol for *O. onites*).

Results from this study contribute to the demand by both consumers and regulatory bodies for improved methodologies and reliable data for assuring oregano genuineness and for revealing the wide variety of fraudulent practices affecting this aromatic herb.

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P42

A NOVEL APPROACH FOR THE GREEN EXTRACTION OF FORSKOLIN FROM *Coleus forskohlii* ROOT BY THE USE OF BIO-SOLVENTS

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There is currently a growing interest in obtaining bioactive ingredients of plant origin through new, more sustainable and green technologies for their use as functional ingredients or food supplements. *Coleus forskohlii*, is a medicinal plant, endemic to tropical and subtropical areas of Asia, Africa and South America, with multiple beneficial properties (e.g. anti-obesity and anti-thrombotic) associated with forskolin, its main bioactive phytochemical [1]. Thus, different food supplements based on its root extracts, usually standardized in forskolin, are commercialized. These extracts are typically obtained using organic solvents such as methanol [2].

In this study we have demonstrated the effectiveness of *in silico* approaches in the selection of new, more efficient, eco-sustainable and safe solvents, such as Natural Deep Eutectic Solvents (NADES) or biomass-derived bio-solvents (terpenoids), to carry out extraction processes of forskolin from *C. forskohlii* root. Among terpenoids, thymol and carvacrol exhibited the highest solvent capacities for forskolin extraction. As thymol is solid at room temperature, its potential use as a component of NADES was investigated.

The application of COSMO-RS theory facilitated the design of the most promising thymol based NADES, covering different degrees of hydrophobicity: thymol:butyric acid (1:3; NADES1), thymol:octanoic acid (1:2; NADES2) and thymol:decanoic acid (1:2; NADES3). A good agreement was found between the predicted theoretical values and those obtained through experimental characterization techniques, such as differential scanning calorimetry (DSC) and infrared spectroscopy (IR). HPLC-MS analysis of the extracts obtained with the different bio-solvents revealed that the highest extraction yields of forskolin and its bioactive isomer isoforskolin were obtained with carvacrol and NADES1, with 0.52 and 0.44 mg g^{-1} respectively, and higher than that obtained with methanol (0.30 mg g^{-1}). The good results obtained with these biosolvents make them of interest for their potential application in the food industry, in addition to offering ecological advantages over traditional solvents, reducing environmental impact and health risks.

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FIA-MS METHODOLOGY FOR THE FAST DETECTION OF ADULTERANTS IN DAMIANA (*TURNERA DIFFUSA*) EXTRACTS

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Among the food supplements (FS) available on the market, those intended for sexual health are one of the most adulterated, with phosphodiesterase-5 inhibitors (iPDE-5), prescription drugs for the treatment of erectile dysfunction, being the main adulterants [1]. Most of these FS are formulated using plant extracts known for their stimulant or aphrodisiac effects, such as Damiana (*Turnera diffusa*) leaf extract. Although several analytical methods have been developed for the determination of PDE5i in FS [2], most of them involve a chromatographic separation step. Therefore, in this work, as a fast and sensitive alternative to detect and reliably quantify PDE5i in damiana extracts, a new methodology based on Flow Injection Analysis–Mass Spectrometry (FIA-MS) was optimized and validated.

A Box-Behnken experimental design was used for the optimization of MS parameters, paying special attention to those affecting electrospray ionization (drying gas temperature, nebulizer pressure and fragmentor voltage). After optimization of the individual responses of the four PDE5i considered (sildenafil, tadalafil, vardenafil and avanafil), a multiple response analysis was used to obtain the optimal conditions to maximize the abundance for all these PDE5i. Moreover, influence of mobile phase additives, like formic acid percentage and addition of formate salts, and capillary voltage were also evaluated. Finally, the optimized method was validated by using an intentionally adulterated damiana extract sample with the four selected PDE5i prepared in the laboratory. Positive electrospray ionization mode was selected as no signal for none of the four PDE5i in negative mode was observed. Regarding ionization parameters, avanafil and vardenafil responses were favored by low nebulization pressure (20 psi), high gas temperature (350 °C) and relatively high fragmentor voltage (190 V). Similarly, low nebulization pressure (20 psi) and high gas temperature (350 °C) also maximized tadalafil response, but lower fragmentor voltage was needed (113 V). On the contrary, vardenafil response was improved by high nebulization pressure (50 psi), slightly lower gas temperature (325 °C) and lower fragmentor voltage (98 V). The optimal parameters given by multiple response methodology were 20 psi for nebulization pressure, 350 °C as gas temperature and 136 V as fragmentor voltage. The optimized FIA-MS method was then validated, with good linearity, repeatability values below 5% RSD, absence of matrix effect and LOD and LOQ below 28 and 91 ng/g, respectively. This methodology could be a fast and reliable alternative for the quality control of damiana extracts.

Acknowledgements

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IN-DEPTH ANALYSIS OF THE PHYTOCHEMICAL AND BIOACTIVE PROFILE OF 12 SPECIES OF ADRIATIC ALGAE BY MSPD-UHPLC-QTOF

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The significant relationship between the algal phytochemical profile and the habitat conditions is well known. Salinity changes, high solar radiation levels, and adverse climatic conditions induce the release of bioactive compounds by these macro-organisms. In this context, the Adriatic Sea is notable for its high solar irradiance, a high salinity gradient, and for being a hotspot in terms of multiple climatic hazards. Thus, although a relevant concentration of the phytochemical arsenal of macroalgae inhabiting the Adriatic Sea can be assumed, the characterisation of its diverse species has been little explored. In this context, this work proposes the exploration of 12 Adriatic Sea algal species, including 7 brown algae (*Ericaria amentacea*, *Fucus virsoides*, *Cutleria multifida*, *Cystoseira compressa*, *Cystoseira corniculata*, *Gongolaria barbata*, and *Padina pavonica*), 3 green algae (*Codium adhaerens*, *Codium vermilara*, and *Ulva lactuca*) and 2 species of red algae of the genus *Asparagopsis* catalogued as invasive, but with an important bioactive potential, so their use in industrial applications could be a suitable strategy to reduce their population. In addition, different harvesting areas of these macroalgae are evaluated, analysing the impact of modifications in their habitat. In accordance with previous research by the authors[1], matrix solid phase dispersion (MSPD) is proposed as an extraction technique, using solvents generally recognised as safe (GRAS) to obtain algal extracts without prior drying pre-treatments. This new approach is evaluated by characterising the bioactive profile of the endemic seaweed *Fucus virsoides* in the pre- and post-spray-drying stages. The extracts were analysed by quantifying their total polyphenolic content and antioxidant activity using DPPH and ABTS methods. Similarly, a characterisation of the phenolic profile of these macroalgae is performed by HPLC-MS/MS liquid chromatography. In addition, an in-depth analysis by UHPLC-QToF is proposed in the comparative analysis of all species, using a non-targeted approach for the identification of new compounds. These results are presented as a database on the bioactivity and analytical profile of these mostly understudied algae, showing their potential as a natural source of functional compounds.

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P45

RECOVERY OF PROTEINS FROM GRAPEFRUIT PEELS AS A SOURCE OF BIOACTIVE PEPTIDES: ULTRASOUND ASSISTED EXTRACTION, NATURAL DEEP EUTECTIC SOLVENTS AND PRESSURIZED LIQUID EXTRACTION

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Citrus fruits are widely cultivated in many regions of the world and are renowned for their medicinal and therapeutic properties [1]. Citrus processing, mainly focused on juice production, generates substantial waste in the form of peel, seeds, or pomace, among others, which can reach a 67% of the total production [1-3]. Since these residues can contain significant amounts of high added-value compounds, the development of green extraction strategies enabling their recovery is of great interest since they contribute to the “zero waste” principle and circular economy.

The main aim of this work was to develop sustainable methodologies for the extraction of proteins from grapefruit peels as a mean for their revalorization and to investigate the potential of protein extracts obtained as a source of bioactive peptides. Different extraction strategies were proposed based on ultrasound-assisted extraction, using as extractants a buffer solution or a natural deep eutectic solvent (NaDES), and pressurized liquid extraction. Protein extracts were hydrolyzed using two enzymes, and different *in vitro* assays were performed to evaluate the biological activities of the peptide hydrolysates. Finally, the most active peptide hydrolysates were characterized using UHPLC-QTOF-MS.

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EXTRACTION AND CHARACTERIZATION OF BIOACTIVE CARBOHYDRATES AND PHENOLICS FROM PHYTOPLANKTON HOLOBIONTS

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In recent years, interest in microalgal research and investment have increased as they represent a novel source of high value bioactive compounds (carbohydrates, phenolics, lipids, etc.) with antioxidant, anti-ageing, or antibacterial properties, and with applications in different industries (e.g. cosmetics) [1]. Moreover, the use of microalgal consortia (also known as phytoplankton holobionts), constituted by different species of microalgae or by microalgae and bacteria, are gaining more importance, as they can produce different bioactive molecules due to cooperative interactions between the co-cultured microorganisms [2]. However, these consortia are still scarcely applied in the cosmetic and nutraceutical fields, being necessary at first instance the characterization of their bioactive composition. Towards a zero-waste approach, in the present work, the simultaneous extraction of phenolic compounds and carbohydrates from two different microalgae consortia was optimized. These consortia were based on Kamptonema sp., Nannochloropsis oculata, Tetraselmis sp. and Chlorella sp. (holobiont 1) and on Spirulina sp. and Chlorella vulgaris (holobiont 2). Moreover, a multianalytical approach was followed for the characterization of extracts. First, the efficiency of different solvents for the extraction of target bioactives was evaluated; water was selected as the most effective solvent for both consortia. Then, a Box-Behnken experimental design was performed considering extraction time, temperature and ratio between biomass and solvent as independent factors. Extracts obtained under optimal extraction conditions (30°C, 60 min and 0.01 g of biomass mL-1 for holobiont 1 and 51°C, 60 min and 0.02 g of biomass mL-1 for holobiont 2) were treated with citric acid to precipitate proteins. GC-MS analyses of carbohydrates, before and after trifluoroacetic acid hydrolysis, and subsequent derivatization, allowed the identification of their monomeric composition, while size exclusion chromatography (SEC) with light scattering detection (ELSD) provided information about their molecular weight distribution. Other complementary techniques such as infrared spectroscopy, nuclear magnetic resonance and UV spectroscopy were used to get more information about polysaccharide structures. Reverse phase liquid chromatography coupled to mass spectrometry (RPLC-MS) analyses were also used for the determination of phenolic compounds. These studies constitute an advance in the knowledge of these holobionts which is essential for the development of new applications in the cosmetic and nutraceutical fields, among others.

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SUBCRITICAL WATER EXTRACTION COMBINED WITH ENZYMATIC ASSISTED EXTRACTION FOR PROTEIN RECOVERY FROM LIME PEELS. CHARACTERIZATION OF PROTEIN HYDROLYSATES

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Reusing residues or byproducts from the food industry to obtain high-added value compounds contributes to the sustainability of the food chain and decreases the negative environmental impact derived from the elimination of food waste. Citrus industry generates a big amount of residues such as pomace, peels or seeds that contain different bioactive compounds. The recovery of these compounds requires the development of sustainable strategies based on the use of techniques which respect the principles of green chemistry. The extraction of proteins from citrus peels using sustainable techniques has scarcely been studied.

The main objective of this work was to develop sustainable methodologies to recover proteins from lime peels. With this aim, enzyme-assisted extraction (EAE) was firstly investigated. Seventeen polysaccharidase enzymes were assayed, achieving a high extraction yield for proteins under the most favorable conditions, although requiring long extraction times. Subcritical water extraction (SWE) was then used to reduce this extraction time while keeping a suitable protein recovery. Under optimized conditions, established using an experimental design, 63 % of the proteins from lime peels could be extracted by SWE at a significantly reduced extraction time. Trying to meet both a high protein recovery and a reduced extraction time, EAE and SWE were simultaneously combined. This strategy enabled to reach a high extraction of proteins (91 %) in a considerable short analysis time. Moreover, it presented a significantly higher recovery of proteins and improved sustainability than the previous one developed by our research team using pressurized liquid extraction with a water-ethanol mixture as solvent [1]. The obtained protein extracts from lime peels were hydrolyzed using alcalase and thermolysine enzymes and hydrolysates were characterized through the evaluation of their antioxidant, antihypertensive, and antimicrobial activities. Peptides were identified in the most active hydrolysates by UHPLC-Q-TOF-MS.

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COMPARISON OF CHROMATOGRAPHIC METHODS FOR THE ANALYSIS OF HYDROXYCITRIC ACID IN *Garcinia cambogia* EXTRACTS

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Garcinia cambogia is a plant native to India, whose fruit, previously dried and smoked (known as kudam puli), has been widely used for culinary purposes, as it adds flavor to food. In addition, numerous health benefits (e.g. overweight control) have been attributed to the extracts of this fruit associated with their (-)-hydroxycitric acid [(-)-HCA] content [1]. Analysis of this molecule is usually carried out by reverse phase liquid chromatography with ultraviolet detection (RPLC-UV) [2] or by gas chromatography coupled to mass spectrometry (GC-MS) [3]. However, the small size and polar character of the HCA molecule leads to a poor resolution in RPLC, while its low volatility makes its derivatization mandatory for GC analyses, which is not straightforward considering that during this procedure (-)-HCA may degrade or cycle into its lactone.

At the sight of these antecedents, the aim of this work was the optimization of sample preparation and operating conditions of both LC-UV and GC-MS methods for the analysis of (-)-HCA in different kudam puli samles. Both procedures have been compared and advantages and disadvantages of both have been discussed.

To avoid the lactonization or isomerization of (-)-HCA during extraction from kudam puli samples, different solvents, temperatures and times were evaluated. The derivatization conditions of the extracts were optimized for GC-MS, while different stationary phases (both for RP and hydrophilic interaction liquid chromatography modes) and mobiles phases were tested for LC-UV analyses. Once optimal conditions were chosen, both methods were validated. Although good reproducibility and accuracy for (-)-HCA analysis was obtained irrespective of the method considered, a better resolution of this acid from other compounds present in Garcinia was achieved by GC-MS. However, special care should be taken during the required derivatization to avoid (-)-HCA transformation or degradation reactions.

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DETERMINATION OF MOSH AND MOAH BY GCxGC-TOFMS

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Nowadays across the European Union food contamination by mineral oils from production processes and packaging is becoming a serious problem for public health institutions and governments.

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

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

The combination of two different polarity columns led to effective separations between compound families, identifications within families were easily reached by high acquisition rates TOFMS systems and ChromaTOF software classification capabilities defined chromatogram regions to clearly locate each compound family.

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PROFILING BLACK OAT AVENANTHRAMIDES AND POLYPHENOLS

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Oats are the fifth most important cereal in the world [1]. The three main oat species cultivated are *Avena sativa*, *A bizantina* and *A strigosa* (Black Oat). In Spain, the cultivation of *A strigosa* was concentrated in Galicia although it has been suffering an important regression for decades associated with the abandonment of the countryside. However, in recent years, its cultivation has increased steadily at national level, according to MAPA statistics [2]. A multi-level exploration to promote the cultivation of *A strigosa* as an alternative crop on organic farms to produce functional foods has been proposed [3]. However, there is very little data integrating agronomic behaviour and analytical composition. In particular, the traditional Galician varieties have not been studied in depth and their use for derived products of high functional value has not been tested.

Oats are rich in antioxidants, including vitamins E, phenolic acids, flavonoids, phytosterols, and avenanthramides (AVNs), a family of nitrogen-containing phenolic compounds which are unique to oats and one of the main active functional components. In this context, we have developed an ultrasound-based extraction (UAE) method for AVNs, together with a mixed characterization based on *target* analysis (of the three most known avenatramides, AVA, AVB and AVC) by UPLC-MS/MS, and *pseudotarget* analysis via UHPLC-QToF for the determination of 6 additional AVNs to be included in the target method based on QqQ detection (MRM), along with seven further polyphenols.

This work is part of the *AveaMoura project*, whose objective is the upgrading of the traditional varieties of Galicia through a study of multiple uses in food and cosmetics. Hence, the developed methodology is applied to 5 traditional varieties of *A strigosa* and one variety of the wild cultivated species, *Xoio*, grown in different environments.

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PHYTOCHEMICAL AND ANTIOXIDANT COMPOSITION OF *QUERCUS* ACORN EXTRACTS OBTAINED BY MATRIX SOLID-PHASE DISPERSION

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Oak (*Quercus* spp.) acorns are used in animal feed and in the treatment of specific diseases due to their nutritional value and high content of bioactive compounds[1]. The aim of the present work is to investigate and compare polyphenolic compounds and antioxidant activity of *Quercus ilex* and *Quercus robur* acorn extracts. This is performed using the matrix solid-phase dispersion (MSPD) extraction process, in an environmentally friendly way with different generally recognised as safe (GRAS) solvents[2]. The GRAS solvents considered were ethanol, acetone, ethyl lactate, and propylene glycol. Total phenolic content (TPC) and antioxidant activity (DPPH and ABTS scavenging test) were determined spectrophotometrically. The different antioxidant data obtained by two approaches are discussed. All *Quercus robur* extracts show better results than *Quercus ilex* in both total phenol content and antioxidant activity, the highest results being obtained with ethyl lactate, 73.46 mgGAE g^{-1} DW and 0.81 mmolTE g^{-1} DW, respectively. These results demonstrate the correlation between total phenol content and antioxidant activity, and that free radical scavenging is concentration dependent. Individual quantification of the polyphenols was performed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) being the major compounds gallic acid, ellagic acid, catechin, quercetin and gallotannins in all extracts. In addition, a non-targeted analysis by ultra high-performance liquid chromatography quadrupole time-of-flight (UHPLC-QToF) is carried out for a qualitative comparison of the two species. MSPD, for the first time applied to acorns, has proven to be a good alternative to conventional processes for obtaining extracts rich in bioactive compounds.

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NOVEL TRIPLE QUAD APPROACHES FOR ROBUST AND RELIABLE ANALYSIS OF PFAS IN FOOD MATRICES WITH ULTIMATE SENSITIVITY

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PFAS analysis even when is regulated to a targeted list of compounds inherit many difficulties related with the low levels of quantitation and the blank management in a routine lab.

In this poster we will show the remarkable performance of the new LCMS EVOQ DART-TQ+ system, when performing a high demanding PFAS analysis for ultimate sensitivity and short analysis times, in difficult matrices. Also, we will describe the workflow including strategies to avoid blank contamination in LCMS

To help improving the capabilities of any laboratory involved in food safety, environmental, water ARACELIanalysis or regulation control requiring the best performance available for target analysis.

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IDENTIFICATION OF KEY MARKERS REVEALING THE STERILIZATION IMPACT ON PAPRIKA: LIQUID-CHROMATOGRAPHY-HIGH-RESOLUTION MASS SPECTROMETRY AS A POWERFUL TOOL

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Paprika (*Capsicum annuum*) is a popular spice known for its distinctive flavor and sensory qualities [1]. However, during the production of spices and herbs, there is a risk of contamination by harmful microorganisms. Consequently, heat sterilization, which avoids the use of chemicals and radiation, has become crucial for ensuring microbiologically safe condiments in the European market [2]. This study presents an innovative untargeted metabolomics approach to evaluate the impact of sterilization on the metabolomic composition of paprika. This study applied ultra-high performance liquid chromatography (UHPLC) combined with quadrupole-Orbitrap-high-resolution mass spectrometry (HRMS) for paprika fingerprinting. Paprika samples were prepared using a straightforward solid-liquid extraction method with sonication with a methanol-water mixture (80:20 *v/v*). A supervised orthogonal partial least squares discriminant analysis (OPLS-DA) model was then developed based on UHPLC-HRMS paprika fingerprints to distinguish between sterilized and untreated samples. This model demonstrated excellent sample clustering and high-quality parameters ($R^2Y = 0.988$ and $Q^2 = 0.904$), accurately classifying all external samples. Additionally, this methodology led to the identification of 19 significant metabolites that can differentiate between sterilized and non-sterilized paprika. Key findings included a significant decrease in fatty acids such as stearidonic acid due to sterilization, along with an increase in other metabolites such as DL-malic acid and flazin, which can serve as specific markers of sterilized paprika. This study opens the door to new metabolomics strategies for verifying the integrity of paprika and other valuable spices, with a particular focus on the relatively unexplored area of sterilization processes.

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NON-TARGETED METABOLOMICS FOR THE AUTHENTICATION AND DIFFERENTIATION OF HONEY TYPES: A COMPARATIVE STUDY OF COMMERCIAL AND OPEN-SOURCE DATA PROCESSING TECHNIQUES

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Honey, a natural foodstuff rich in carbohydrates, is highly appreciated by its nutritional value and sweet taste, but also by its pleasant and characteristic aroma profile that plays a relevant role in honey selection by consumer (Quintanilla-López, 2022). Pollen and physicochemical analysis are not always the best way to identify honey's origin. In some cases where lavender consists of hybrid varieties, pollen may be underrepresented. Therefore, other tests are required, such as organoleptic analysis and the identification of specific volatile compounds (Escriche, 2017).

This study aims to explore the capabilities of non-targeted metabolomics in identifying volatile biomarkers in Lavender honey (Lavender and Lavandin) and distinguish them from markers found in Thyme and Cantueso honey, thereby ensuring the quality and origin of honey products available in the market. For this purpose, a GC-QExactive hybrid quadrupole-Orbitrap mass spectrometer was employed. Volatile isolation was done using a fully automated SPME autosampler (Thermo) provided with a 75 µm divinylbenzene/carboxen/ polydimethylsiloxane (DVB/CAR/PDMS) SPME fiber. The dataset comprised 52 samples, including 23 Lavender honey, 10 Thyme honey, 9 Lavandin honey, 7 multifloral honey, 3 Cantueso honey, and 5 samples from Lebanon. The samples underwent a standardized treatment process, including dissolution in MilliQ water and addition of NaCl, followed by HS-SPME at 60°C for 30 minutes. The extracted volatile compounds were thermally desorbed and analyzed using GC-EI-HRMS.

Data processing involved both commercial (Compound Discoverer) and open-source (MS Dial) software to ensure comprehensive extraction of sample components (Rivera-Pérez, 2024). The identification of selected biomarkers was performed using the NIST mass spectral database and Kovats retention indices. Subsequent univariate and multivariate analyses were conducted using EzInfo (commercial) and MetaboAnalyst (open-source) to select potential biomarkers. Principal component analysis (PCA) and partial least squares discriminant analysis (PLS-DA) facilitated the classification of honey types, while orthogonal partial least squares discriminant analysis (OPLS-DA) and S-plots enabled the identification of characteristic markers, allowing to understand and compare the results obtained from both commercial and open-source software for data processing and analysis.

This study demonstrates the potential of GC-EI-HRMS combined with advanced statistical data processing to differentiate honey types based on their volatile profiles. The identified biomarkers can serve as reliable indicators for the authentication and quality control of Lavender honey, contributing valuable insights to the honey industry and the broader field of food metabolomics. The analysis revealed distinct volatile profiles and identified new and different markers when comparing results obtained from commercial software and open-source software, demonstrating the complementary strengths of both approaches in characterizing honey types.

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P55

ENHANCED CLASSIFICATION OF TEA VARIETIES USING HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY AND GLOBAL RETENTION MODELS

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As a result of their metabolic processes, medicinal plants generate bioactive molecules with significant implications for human health. These compounds are used in disease treatment or in the development of pharmaceutical products [1]. Chromatographic fingerprints, which are chromatograms from samples eluted under wide-scan gradients [2], reveal the diversity of chemical constituents and are nowadays crucial for authenticating and categorising medicinal plants. In this research, an optimised gradient program, based on the use of global models fitted without the need of standards, was applied to improve chromatographic resolution [3,4]. This gradient was applied to classify samples from six tea varieties. The classification study enhanced a previous one [5] by improving the data treatment and increasing the number of samples and replicates for each variety. The analysis involved 96 chromatograms from 45 commercial tea samples, including green, white, red, black, and oolong teas, as well as rooibos samples. To evaluate classification viability, Principal Component Analysis (PCA), *k*-Means Clustering, and Partial Least Squares-Discriminant Analysis (PLS-DA) were applied, considering different data sets. Peak fluctuations were corrected using Correlation Optimised Warping (COW), and elution bands as well as band ratios, where the maximal signals in defined elution regions were measured. The COW alignment enabled the processing of the original signals (baseline corrected), achieving sharper classifications of the six varieties of tea. The limitations found in the classification were reasonable given the multiplicity of factors affecting product composition, including manufacturing operations, like drying, fermentation, growth conditions, geographical location, ageing, and others, which significantly impact product variability.

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APPLICATION ROBUSTNESS OF THE 6495 TRIPLE QUADRUPOLE LC/MS SYSTEM FOR NON-STOP PESTICIDE ANALYSIS IN BLACK TEA MATRIX

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System robustness is of utmost importance especially when analyzing samples for routine, in-production, type of analysis. Additionally, when evaluating samples for meaningful scientific results, analysis of a large population of samples is necessary for good population statistics.

The new 6495 triple quadrupole LC/MS system (G6495D) is equipped with VacShield and iFunnel technology that aims to provide high sensitivity and high-performance analysis while being robust and rugged enough to withstand the effects of deposition from a complex and dirty matrix.

- VacShield –ion injector capillary removal mechanism that enables quick routine-maintenance, reduces downtime, and preserves system stability.

- iFunnel Technology – a dual-staged stacked ring ion funnel used to compress and concentrate the ion beam. Innovations within the iFunnel evacuate matrix components while maintaining injection-to-injection MRM precision.

- Instrument Intelligence – built into the overall system architecture to monitor and ensure that the instrument is in good operating condition.

Compared to non-iFunnel systems, the 6495 LC/TQ provides about 10x improvement in signal while providing superior injection-to-injection measurement robustness and precision at sub-millisecond dwell times.

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