SECyTA 2016
SEVILLA
2-4 NOV.

BOOK OF ABSTRACTS - LIBRO DE RESÚMENES

XVI REUNIÓN CIENTÍFICA DE LA SOCIEDAD ESPAÑOLA DE CROMATOGRAFÍA Y TÉCNICAS AFINES - SECyTA 2016

ADVANCES IN CHROMATOGRAPHY AND RELATED TECHNIQUES

XVI SCIENTIFIC MEETING OF THE SPANISH SOCIETY OF CHROMATOGRAPHY AND RELATED TECHNIQUES - SECyTA 2016

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– 2016 –

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XVI REUNIÓN CIENTÍFICA DE LA

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XVI SCIENTIFIC MEETING OF THE

SPANISH SOCIETY OF CHROMATOGRAPHY

AND RELATED TECHNIQUES · SECyTA 2016

Editors:

J.A. González-Pérez, G. Almendros, F.J. González-Vila and J.M. de la Rosa

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SECyTA2016: PROGRAMME AT A GLANCE

	Wednesday, November 2	Thursday, November 3		Friday, November 4
8:00	**Registration**			
8:45	**Opening Ceremony**	**Thursday, November 3**		
9:00	**Plenary Lecture** PL-1. S. De Saeger	**Plenary Lecture** PL-3. E. M. Thurman		**Friday, November 4**
9:40	**Plenary Lecture** PL-2. J. E. Spangenberg	**Plenary Lecture** PL-4. E. Moyano	9:30 9:50	**Oral Session 3** O-CPA-1 O-CPA-2
10:20	**Coffee break & Exhibition**	**Coffee break & Exhibition**	10:10	**Coffee break & Exhibition**
10:40	**Poster Session 1** Food Analysis (FA)	**Poster Session 3** Environmental Analysis (ENV), New Developments in Instrumentation (NDI) & Sample Preparation (SP)	10:30 10:50 11:10 11:30	**Oral Session 4** O-SP-1 O-SP-2 O-SP-3 O-SP-4
11:30 11:50 12:10 12:30 12:50 13:10	**Oral Session 1** O-FA-1 O-FA-2 O-FA-3 O-FA-4 O-NP-1 O-NP-2	**Oral Session 2** O-ENV-1 O-ENV-2 O-ENV-3 O-NDI-1 O-NDI-2 O-OT-1	11:50 12:30 13:00	**Closing Plenary Lecture** PL-5. M. J. González **Closing Ceremony and Awards** **Farewell Cocktail**
13:30	**Lunch & Lunch Seminars** (Agilent Technologies & LECO Instr.)	**Lunch & Lunch Seminar** (Bruker Daltonics)	14:00	**Lunch Seminar** (Frontier Lab)
15:00	**Poster Session 2** Clinical and Pharmaceutical Analysis (CPA), Natural Products (NP) & Omics Techniques (OT)	**Poster Session 4** Fundamentals and Chemometrics (FCH), Isotopic Analysis (IA) & Other Applications (OA)		
15:50 15:55 16:00 16:05 16:10 16:15	**Poster Flash Session 1** P-FA-4 P-FA-22 P-FA-30 P-CPA-1 P-CPA-9 P-OT-10	**Poster Flash Session 2** P-ENV-5 P-ENV-21 P-IA-3 P-SP-8 P-FCH-2 P-OA-5		
16:20	**Coffee break & Exhibition**	**Coffee break & Exhibition**		
16:40 16:50 17:00 17:10 17:20 17:30 17:40 17:50 18:00 18:10	**Young Scientists Session 1** OJ-FA-1 OJ-FA-2 OJ-FA-3 OJ-NP-1 OJ-CPA-1 OJ-CPA-2 OJ-CPA-3 OJ-OT-1 OJ-OT-2 OJ-OA-1	**Young Scientists Session 2** OJ-ENV-1 OJ-ENV-2 OJ-ENV-3 OJ-ENV-4 OJ-ENV-5 OJ-NDI-1 OJ-NDI-2 OJ-SP-1 OJ-SP-2 **SECyTA General Assembly**		
19:30	**Social Event**: Reales Alcázares & Real Fábrica Tabacos			
20:30		**Social Event:** Conference Dinner Hacienda Montecarmelo		

CONTENT

Bienvenida

Estimado Colega,

La reunión de la Sociedad Española de Cromatografía y Técnicas Afines (SECyTA) se celebra cada año y constituye sin duda el congreso de mayor prestigio en España en su ámbito de interés. El Grupo de materia orgánica en suelos y sedimentos (MOSS) del Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC) asume la responsabilidad de organizar esta XVI edición de la Reunión Científica SECyTA2016 que se celebrará entre los días 2 al 4 de noviembre.

Es nuestra intención que en esta edición se mantenga la tradición como foro científico de excelencia para la presentación y discusión de investigaciones punteras sobre técnicas de separación cromatográfica y afines, así como de sus múltiples acoplamientos y aplicaciones. En estrecha colaboración con la Junta de Gobierno de la SECyTA hemos preparado un programa que esperamos sea atractivo, tanto en los aspectos científicos como en lo social, con la posibilidad también de que disfruten de algunos aspectos de la cultura y la tradición andaluza.

Como en anteriores ediciones la reunión está estructurada en conferencias plenarias impartidas por científicos invitados de reconocido prestigio internacional, comunicaciones orales, que incluye sesiones para jóvenes investigadores, así como sesiones de pósters, presentaciones “flash” y una magnífica exposición comercial. Las sesiones científicas incluirán los últimos avances instrumentales, y nuevas aplicaciones a las técnicas ómicas, ciencias de la salud, farmacología, alimentación, medioambiente, paleoambiente y geoquímica, arqueología, etc.

Queremos destacar aquí el apoyo decisivo de la SECyTA a los investigadores jóvenes mediante la concesión de becas y bolsas de viaje para facilitar su participación activa en el congreso. Además, junto con la empresa BRUKER, la SECyTA concederá los premios “José Antonio García Domínguez” que en ésta su XII edición reconocerán el mérito científico de las comunicaciones presentadas por nuestros jóvenes investigadores.

Finalmente la celebración de esta nueva edición de la reunión de la SECyTA2016 ha sido posible gracias a la participación de más de 150 científicos y técnicos que presentarán un total de más de 170 comunicaciones en forma oral o pósters y al apoyo decisivo del sector empresarial que, como empresas colaboradoras o patrocinadoras, mantienen un compromiso que se renueva año tras año. Hemos contado además con la colaboración de la ETSII y de los Servicios Generales de Investigación (CITIUS-SGI) de la Universidad de Sevilla, del IRNAS-CSIC y del Patronato de los Reales Alcázares de Sevilla, que han facilitado la cesión de sus magníficas instalaciones para la celebración de este congreso.

En nombre del Comité Organizador les transmitimos nuestro sincero agradecimiento y la más cordial bienvenida a Sevilla. Deseamos que las jornadas que pasemos juntos sean muy productivas en lo laboral y agradables en el ámbito social.

Atentamente,

José A. González Pérez	José Mª de la Rosa Arranz	Francisco J. González Vila
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Previous meetings

President/s	*Location*	*Edition*	*Year*
Jordi Mañes	Valencia	I	2001
Manuel V. Dabrio	Barcelona*	II	2002
Amadeo R. Fernández-Alba	Aguadulce	III	2003
Coral Barbas	Boadilla del Monte	IV	2004
Juan Cacho	Barcelona*	V	2005
Ana Gago	Vigo	VI	2006
Ana María García Campaña	Granada	VII	2007
Joan O. Grimalt	Barcelona*	VIII	2008
Carmen Dorronsoro	San Sebastián	IX	2009
Yolanda Picó	Valencia	X	2010
Elena Domínguez	Barcelona*	XI	2011
Rosa María Marcé	Tarragona	XII	2012
Miguel Ángel Rodríguez & Alejandro Cifuentes	Puerto de la Cruz	XIII	2013
María José González	Barcelona*	XIV	2014
Juan V. Sancho & Joaquín Beltrán	Castellón de la Plana	XV	2015
José A. González-Pérez, José Mª de la Rosa & Francisco J. González-Vila	Sevilla	XVI	2016

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

INVITED SPEAKERS

María José González Carlos
Department of Instrumental Analysis and Environmental Chemistry (AIQA)
Institute of General Organic Chemistry, The Spanish National Research Council (IQOG-CSIC), Madrid, Spain
"Advances in environmental chemistry linked to separation techniques development: my personal experience"

Earl Michael Thurman
Center for Environmental Mass Spectrometry (CEMS), University of Colorado, Boulder, U.S.A.
"Analytical methods for the study of hydraulic fracturing fluids and waters"

Jorge E. Spangenberg
Institute of Earth Surface Dynamics (IDYST),
University of Lausanne, Switzerland
"Effects of water stress on vine leaf surface waxes and wine VOCs: a GC-MS/FID and GC-IRMS study"

Sarah De Saeger
Department of Bioanalysis, Faculty of Pharmaceutical Sciences, Ghent University, Belgium
"UHPLC-MS-based metabolomics strategies to investigate known and novel fungal secondary metabolites"

Encarnación Moyano
Department of Analytical Chemistry. Faculty of Chemistry, University of Barcelona, Spain
"Tandem or high resolution mass spectrometry? That's the question in environmental and food analysis"

SCIENTIFIC AND SOCIAL PROGRAMME

Wednesday, November 2

Registration

08:00 Registration and Symposium Secretary open

Opening Ceremony and Plenary Lectures

08:45 Opening Ceremony

Miguel A. Ferrer Baena – Institutional Coordinator in Andalucía
CSIC
José Enrique Fernández Luque – Director
IRNAS-CSIC, Sevilla
Francisco Javier Santos Vicente – President of SECyTA
University of Barcelona
José Luis Sevillano Ramos – Director
ETSII-University of Sevilla
José Antonio González Pérez – Chairman
IRNAS-CSIC, Sevilla
José Mª de la Rosa Arranz – Co-Chairman
IRNAS-CSIC, Sevilla
Francisco Javier González Vila – Scientific Committee Chairman
IRNAS-CSIC, Sevilla

09:00 Opening Plenary Lectures

Session chairs: Ana Mª García Campaña – *University of Granada*
José Antonio González Pérez – *IRNAS-CSIC, Sevilla*

09:00 **PL-1** UHPLC-MS-BASED METABOLOMICS STRATEGIES TO INVESTIGATE KNOWN AND NOVEL FUNGAL SECONDARY METABOLITES
Sarah De Saeger
Department of Bioanalysis, Faculty of Pharmaceutical Sciences, Ghent University, Belgium

09:40 **PL-2** EFFECTS OF WATER STRESS ON VINE LEAF SURFACE WAXES AND WINE VOCS: A GC-MS/FID AND GC-IRMS STUDY
Jorge E. Spangenberg
Institute of Earth Surface Dynamics, University of Lausanne, 1015, Lausanne, Switzerland

10:20 Coffee Break & Exhibition

10:40 Poster Session 1: (detail in page 25)
Food Analysis (FA)

11:30 Oral Session 1: Food Analysis (FA) & Natural Products (NP)

Session chairs: María José González Carlos – *IQOG-CSIC, Madrid*
Juan Vicente Sancho Llopis – *University Jaume I, Castelló*

11:30 O-FA-1 DETERMINATION OF BISPHENOLS WITH ESTROGENIC ACTIVITY IN BABY FOOD SAMPLES BY SOLID-LIQUID EXTRACTION AND CLEAN-UP WITH DISPERSIVE SORBENTS FOLLOWED BY GAS CHROMATOGRAPHY TANDEM MASS SPECTROMETRY ANALYSIS

María Teresa García-Córcoles[(1)], Rocío Rodríguez-Gómez[(1)], Alberto Zafra-Gómez[(1)], Ana Rivas[(2)], Fátima Olea-Serrano[(2)], José Luis Vílchez[(1)]
[(1)] Research Group of Analytical Chemistry and Life Sciences, Department of Analytical Chemistry, Campus of Fuentenueva, University of Granada, E-18071 Granada, Spain; [(2)] Research Group on Nutrition, Diet and Risk Assessment, Department of Nutrition and Food Science, University of Granada, Cmpus of Cartuja s/n, 18071, Granada, Spain

11:50 O-FA-2 BENEFITS OF USING MASS DETECTION FOR ROUTINE AMINO ACID ANALYSIS

Eric S.E. van Beelen, Ben Dugas
Waters Corporation, St Quentin, France

12:10 O-FA-3 VALORIZATION OF BLACK CHOKEBERRIES (*Aronia melanocarpa*) POMACE AND CHEMICAL CHARACTERIZATION BY COMPREHENSIVE TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY

Lidia Montero[(1)], Tadas Brazdauskas[(2)], Petras R. Venskutonis[(2)], Elena Ibáñez[(1)], Miguel Herrero[(1)]
[(1)] Foodomics Laboratory, Institute of Food Science Research (CIAL, CSIC), Nicolás Cabrera 9, 28049 - Madrid, Spain; [(2)] Kaunas University of Technology, Department of Food Science and Technology, Radvilenu pl. 19, LT-50254, Kaunas, Lithuania

12:30 O-FA-4 DEVELOPMENT OF LC-MS/MS METHODS FOR THE SIMULTANEOUS QUANTIFICATION OF MYCOTOXINS IN MILK

Myra Evelyn Flores-Flores, Elena González-Peñas
Faculty of Pharmacy and Nutrition, University of Navarra. C/ Irunlarrea 1, 31008, Pamplona, Navarra, Spain

12:50 O-NP-1 CHROMATOGRAPHIC METHODS FOR NANNOCHLOROPSIS GADITANA MICROALGAE EXTRACTS' PROFILING

Bienvenida Gilbert-López, Natalia Pleite, Jose Antonio Mendiola, Miguel Herrero, Alejandro Cifuentes, Elena Ibáñez
Laboratory of Foodomics, Institute of Food Science Research CIAL (CSIC-UAM), Nicolás Cabrera 9, Campus de Cantoblanco, 28049 Madrid, Spain

13:10 O-NP-2 PHLEBODIUM DECUMANUM: CHROMATOGRAPHIC CHARACTERIZATION OF A NATURAL EXTRACT

Laura Martín-Pozo, Alberto Zafra-Gómez, Jose Luís Vílchez
Research Group of Analytical Chemistry and Life Sciences, Department of Analytical Chemistry, University of Granada, Campus of Fuentenueva, E-18071 Granada, Spain

13:30 Lunch & Lunch Seminars (Agilent Technologies & LECO Inst.)

15:00 Poster Session 2: (detail in page 28)
Clinical and Pharmaceutical Analysis (CPA)
Natural Products (NP)
Omics Techniques (OT)

15:50 Poster Flash Session 1:
Food Analysis (FA)
Natural Products (NP)
Clinical and Pharmaceutical Analysis (CPA)
Omics Techniques (OT)

Session chairs: Jordi Díaz Ferrero – *IQS, University Ramon Llull, Barcelona*
María Victoria Ruíz Méndez – *IG-CSIC, Sevilla*

15:50 P-FA-4 GC-MS AND HPAEC-PAD CHARACTERIZATION OF PECTIC OLIGOSACCHARIDES (POS) DERIVED FROM HYDROLYSIS OF CITRUS AND APPLE PECTINS

Carlos Sabater, Álvaro Ferreira, Laura Ruíz-Aceituno, Agustín Olano, Antonia Montilla, Nieves Corzo
Departamento Bioactividad y Análisis de Alimentos. Instituto de Investigación en Ciencias de la Alimentación CIAL, (CSIC-UAM), C/Nicolás Cabrera 9, Campus de Cantoblanco, 28049 Madrid, Spain

15:55 P-FA-22 EVALUATION OF ENDOCRINE DISRUPTING PLASTICISER MIGRATION IN HOUSEHOLD FOOD CONTAINERS

Jorge Sáiz, Belén Gómara
Department of Instrumental Analysis and Environmental Chemistry, Spanish Research Council (IQOG-CSIC), Juan de la Cierva, 3, 28006, Madrid, Spain

16:00 P-FA-30 DETERMINATION OF AMINOGLYCOSIDES IN MILK AND MILK-BASED FUNCTIONAL FOODS BY HILIC-BASED UHPLC-MS/MS AND MOLECULARLY IMPRINTED POLYMER SOLID PHASE EXTRACTION

Ahmed Mohammed Hamed[(1)], David Moreno-González[(2)], Laura Gámiz-Gracia[(1)], Ana M. García-Campaña[(1)]
[(1)] Dept. Analytical Chemistry, Faculty of Sciences, University of Granada, Av Fuentenueva s/n, 18071 Granada, Spain; [(2)] Analytical Chemistry Research Group, Department of Physical and Analytical Chemistry, University of Jaén, 23071 Jaén, Spain

16:05 P-CPA-1 ANALYSIS OF PROSTATE SPECIFIC ANTIGEN (PSA) BY CAPILLARY ELECTROPHORESIS AND TWO-DIMENSIONAL GEL ELECTROPHORESIS. COMPARISON AND COMPLEMENTARITY

Noemi Farina-Gómez[(1)], Sílvia Barrabés[(2)], Angel Puerta[(1)], Esther Llop[(2)], José Carlos Díez-Masa[(1)], Antoinette Perry[(3)], Rafael de Llorens[(2)], Rosa Peracaula[(2)], Mercedes de Frutos[(1)]
[(1)] Department of Instrumental Analysis and Environmental Chemistry, Institute of Organic Chemistry, Spanish Research Council (IQOG-CSIC), Spain; [(2)] Biology Department, Faculty of Science, University of Girona, Spain; [(3)] School of Medicine, Trinity College Dublin, The University of Dublin, Ireland

16:10 **P-CPA-9** STRATEGIES FOR THE DETECTION OF NEW BISGLUCURONIDE, DIGLUCURONIDES AND DICONJUGATED METABOLITES OF ANABOLIC ANDROGENIC STEROIDS

Argitxu Esquivel[1,3], Aristotelis Kotronoulas[1,2], Georgina Balcells[1,3], Jesús Joglar[1,2], Rosa Ventura[1,3]

[1] Bioanalysis Research Group, IMIM, Hospital del Mar Medical Research Institute, Doctor Aiguader 88, 08003 Barcelona, Spain; [2] Department of Biological Chemistry and Molecular Modeling, Instituto de Química Avanzada de Cataluña (IQAC), Consejo Superior de Investigaciones Científicas (CSIC), Jordi Girona 18-26, 08034 Barcelona, Spain; [3] Department of Experimental and Health Sciences, Universitat Pompeu Fabra, Doctor Aiguader 88, 08003 Barcelona, Barcelona, Spain

16:15 **P-OT-10** HIGH RESOLUTION MASS SPECTROMETRY IN THE IDENTIFICATION OF METABOLITES AND TRANSFORMATION PRODUCTS FROM ENROFLOXACIN IN THERMALLY TREATED MILK FROM MEDICATED COWS

Alexandra Junza[1], Javier Saurina[2], Cristina Minguillón[1], Dolores Barrón[1]

[1] Food and Nutrition Torribera Campus, Universitat de Barcelona, Avda. Prat de la Riba 171, 08921 Sta Coloma de Gramenet, Barcelona, Spain; [2] Analytical Chemistry Department, C/ Martí I Franquès 1-11, 08028 Barcelona, Spain

16:20 **Coffee Break & Exhibition**

16:40 **Young Scientists Session 1**

Session chairs: Yolanda Picó García – *University of Valencia*
Francisco Javier Moreno Andújar – *CIAL-CSIC, Madrid*

16:40 **OJ-FA-1** NOVEL GC-MS STRATEGIES FOR THE ACCURATE AND SENSITIVE SPECIATION OF SO_2 IN WINE

Ignacio Ontañón[1], Vanesa Carrascón[1], Mónica Bueno[2], Vicente Ferreira[1]

[1] Laboratorio de Análisis del Aroma y Enología. Departamento de Química Analítica. Facultad de Ciencias. Instituto Agroalimentario de Aragón –IA2- (Universidad de Zaragoza-CITA). C/ Pedro Cerbuna, 12. 50009. Zaragoza, Spain; [2] Instituto de las Ciencias de la Vid y el Vino (UR-CSIC-GR), apartado postal 1042, 26080 Logroño, Spain

16:50 **OJ-FA-2** EXTERNAL CONTROL FOR SPME IN SOLID FOOD SAMPLES: ANALYSIS OF VOLATILE COMPOUNDS IN RAW BEEF

Mónica Bueno[1], Virginia C. Resconi[2], M. Mar Campo[2], Vicente Ferreira[3], Ana Escudero[3]

[1] Instituto de las Ciencias de la Vid y el Vino (UR-CSIC-GR), apartado postal 1042, 26080 Logroño, Spain; [2] Department of Animal Production and Food Science, Faculty of Veterinary, Instituto Agroalimentario de Aragón IA2, Universidad de Zaragoza-CITA, 50013 Zaragoza, Spain; [3] Laboratory for Flavor Analysis and Enology. Department of Analytical Chemistry, Faculty of Sciences, Instituto Agroalimentario de Aragón IA2, Universidad de Zaragoza-CITA, 50009 Zaragoza, Spain

17:00 **OJ-FA-3** COMPREHENSIVE ANALYSIS OF GOAT MILK OLIGOSACCHARIDES

Andrea Martín[1], Jaime Salcedo[2], Daniela Barile[2], Alfonso Clemente[3], Francisco Javier Moreno[4], Ana Isabel Ruiz[1], María Luz Sanz[1]

[1] Instituto de Química Orgánica General (CSIC), Juan de la Cierva, 3 28006 Madrid, Spain; [2] Department of Food Science and Technology, University of California Davis, CA 95616, USA; [3] Estación Experimental del Zaidín (CSIC), Profesor Albareda, 1, 18008 Granada, Spain; [4] Instituto de Investigación en Ciencias de la Alimentación (CSIC-UAM), Nicolás Cabrera, 9 28049 Madrid, Spain

17:10 **OJ-NP-1** USE OF HYBRID QUADRUPOLE-ORBITRAP HIGH-RESOLUTION MASS SPECTROMETRY FOR IDENTIFICATION OF FOUR NOVEL DESTRUXINS PRODUCED BY METARHIZUM BRUNNEUM

Natalia Arroyo-Manzanares[1,2,3], José Diana Di Mavungu[1], Azahara Carpio[2], Inmaculada Garrido-Jurado[4], Lourdes Arce[2], Laura Gámiz-Gracia[3], Ana M. García-Campaña[3], Lynn Vanhaecke[5], Enrique Quesada-Moraga[4], Sarah De Saeger[1]

[1] Laboratory of Food Analysis, Faculty of Pharmaceutical Sciences, Ghent University, Ghent, Belgium; [2] Department of Analytical Chemistry, University of Cordoba, Annex C3 Building, Campus of Rabanales, 14071 Cordoba, Spain; [3] Department of Analytical Chemistry, University of Granada, Campus Fuentenueva s/n, 18071 Granada, Spain; [4] Department of Agricultural and Forestry Sciences, ETSIAM, University of Cordoba, C4 Building, Campus of Rabanales, 14071 Cordoba, Spain; [5] Laboratory of Chemical Analysis, Department of Veterinary Public Health, Faculty of Veterinary Medicine, Ghent University, Ghent, Belgium

17:20 **OJ-CPA-1** SOIL AND PLANT UPTAKE OF PHARMACEUTICALS: ANALYTICAL DETERMINATION

Nicola Montemurro[1,2], Cristina Postigo[2], Antonio Lonigro[1], Sandra Pérez[2], Damia Barceló[2,3]

[1] Dept. of Agricultural and Environmental Science – University of Bari, Via Amendola 165/A – 70126 Bari, Italy; [2] Dept. of Environmental Chemistry, Institute for Environmental Assessment and Water Research (IDAEA-CSIC), Jordi Girona 18-26, 08014 Barcelona, Spain; [3] Catalan Institute for Water Research (ICRA), Parc Cientific i Tecnològic de la Univ. de Girona, Emili Grahit, 101, E-17003 Girona, Spain

17:30 **OJ-CPA-2** COUPLING MICELLAR ELECTROKINETIC CHROMATOGRAPHY WITH MASS SPECTROMETRY USING A VOLATILE SURFACTANT FOR THE THERAPEUTIC MONITORING OF BENZIMIDAZOLES IN ANIMAL URINE

Carmen Tejada-Casado[1], David Moreno-González[2], Francisco J. Lara[1], Monsalud del Olmo-Iruela[1], Ana M. García-Campaña[1]

[1] Dept. Analytical Chemistry, Faculty of Sciences, Univ. Granada, Av. Fuentenueva s/n, E-18071 Granada, Spain; [2] Analytical Chemistry Research Group, Dept. Physical and Analytical Chemistry, Univ. Jaén, 23071 Jaén, Spain

17:40 **OJ-CPA-3** IN-VITRO METABOLISM EVALUATION OF THE TRYPTAMINE 5-MeO-MiPT USING HUMAN LIVER CELLS

D. Fabregat-Safont[1], M. Ibáñez[1], N. Apostolova[2], M. Polo[2], J.V. Sancho[1], F. Hernández[1]

[1] Research Institute for Pesticides and Water, University Jaume I, Avda. Sos Baynat, E-12071, Castellon, Spain; [2] Department of Pharmacology, University of Valencia, Avda Blasco Ibañez n.15-17, 46010 Valencia Spain

17:50 **OJ-OT-1** EARLY METABOLIC CHANGES IN HEPATIC HEPARG CELLS TO ROSEMARY DITERPENES BY METABOLOMICS

Tanize Acunha, Argyro Giannakopoulou, Alberto Valdés, Konstantina Theochari, Alejandro Cifuentes, Virginia García-Cañas, Carolina Simó

Laboratory of Foodomics, Institute of Food Science Research (CIAL, CSIC), Calle Nicolás Cabrera 9, 28049 Madrid, Spain

18:00 **OJ-OT-2** METABOLOMICS INVESTIGATION OF DRUG DEPENDENCE EMPLOYING LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY

Elena Sánchez-López[1], Alberto Marcos[2], Emilio Ambrosio[2], Oleg A. Mayboroda[3], María Luisa Marina[1], Antonio L. Crego[1]

[1] Departamento de Química Analítica, Química Física e Ingeniería Química, Universidad de Alcalá, Ctra. Madrid-Barcelona, Km. 33.600, 28871 Alcalá de Henares, Madrid, España; [2] Departamento de Psicobiología, Universidad Nacional de Educación a Distancia, C/ Juan del Rosal 10, Ciudad Universitaria, 28040 Madrid, España; [3] Center for Proteomics and Metabolomics, Leiden University Medical Center, Leiden, The Netherlands

18:10 **OJ-OA-1** DETECTION, EVALUATION AND CHARACTERIZATION OF NEW STEROID SULFATE METABOLITES

Georgina Balcells[(1,2)], Xavier Matabosch[(1)], Cristina Gómez[(3)], Lorena Garrostas[(1)], Óscar J Pozo[(1)], Rosa Ventura[(1,2)]

[(1)] Bioanalysis Research Group, IMIM, Hospital del Mar Medical Research Institute, Doctor Aiguader 88, 08003 Barcelona, Spain; [(2)] Department of Experimental and Health Sciences, Universitat Pompeu Fabra, Doctor Aiguader 88, 08003 Barcelona, Spain; [(3)] Current address: Experimental Asthma and Allergy Research Unit, The National Institute of Environmental Medicine - Unit for Chemistry II, Department of Medical Biochemistry and Biophysics, Karolinska Institutet, Stockholm, Sweden

19:30 **Social Event**
Visit to the *Reales Alcázare*s & Cocktail at the *Real Fábrica de Tabacos*

Thursday, November 3

08:00 Symposium Secretary Open

Plenary Lectures

Session chairs: Joan Grimalt Obrador – *IDAEA-CSIC, Barcelona*
Juan Vicente Sancho Llopis – *University Jaume I, Castelló*

09:00 PL-3 ANALYTICAL METHODS FOR THE STUDY OF HYDRAULIC FRACTURING FLUIDS
E. Michael Thurman and Imma Ferrer
Laboratory for Environmental Mass Spectrometry, Environmental Engineering, University of Colorado, Boulder, CO, USA

09:40 PL-4 TANDEM OR HIGH RESOLUTION MASS SPECTROMETRY? THAT'S THE QUESTION IN ENVIRONMENTAL AND FOOD ANALYSIS
Encarnación Moyano
Department of Analytical Chemistry, Faculty of Chemistry, University of Barcelona, Spain

10:20 Coffee Break & Exhibition

10:40 Poster Session 3: (detail in page 32)
Environmental Analysis (ENV)
New Developments in Instrumentation (NDI)
Sample Preparation (SP)

11:30 Oral Session 2: Environmental Analysis (ENV), New Developments in Instrumentation (NDI) & Sample Preparation (SP)

Session chairs: José Julio Ortega – *IRNAS-CSIC*
Francisco Javier Santos Vicente – *University of Barcelona*

11:30 O-ENV-1 DETERMINATION OF HIGHLY POLAR PESTICIDES IN LETTUCE AND CELERY BY QUICK POLAR PESTICIDES EXTRACTION METHOD AND DIRECT ANALYSIS IN REAL TIME
Francisco J. Lara[(1)], Danny Chan[(2)], Michael Dickinson[(2)], Antony S. Lloyd[(2)], Stuart J. Adams[(2)], Ana M. García-Campaña[(1)]
[(1)] Dept. of Analytical Chemistry, University of Granada, Av. Fuente Nueva s/n, 18071, Spain; [(2)] Fera Science Ltd, Sand Hutton, York YO41 1LZ, United Kingdom

11:50 **O-ENV-2** UNAMBIGUOUSLY DICERNING HOST RANGE IN THE HOLOPARASITE *Cistanche phelypaea (L.) (Orobanchaceae)* USING PYROLYSIS-COMPOUND SPECIFIC ISOTOPE ANALYSIS (Py-CSIA)

José A. González-Pérez[(1)], Enrique Figueroa[(2)], Enrique Figueroa-Luque[(3)], Teresa Luque[(2)], Laura Cano[(2)], Nicasio T. Jiménez-Morillo[(1)], Francisco J. González-Vila[(1)]
[(1)] IRNAS-CSIC. Avda. Reina Mercedes 10, 41012, Sevilla, Spain; [(2)] Univ. Sevilla, Fac Biol, Dept Biol Vegetal & Ecol, 41080, Sevilla, Spain; [(3)] EBD-CSIC, Cartuja TA-10, Calle Américo de Vespucio, s/n, 41092, Sevilla, Spain

12:10 **O-ENV-3** COMPREHENSIVE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN ATMOSPHERES THAT ARE UNDER INFLUENCE OF THE EMISSIONS FROM A CHLOR-ALKALI PLANT

Barend L. van Drooge, Esther Marco, Joan O. Grimalt
Institute of Environmental Assessment and Water Research (IDÆA-CSIC), c/Jordi Girona 18-26, 08034 Barcelona

12:30 **O-NDI-1** EXPANDING CAPABILITIES OF GC/MS SYSTEMS USING VERTICAL FURNACE PYROLYZER: DEFORMULATION AND IDENTIFICATION OF UNKNOWN POLYMERIC MATERIAL

Michael Soll, Ichi Watanabe
Frontier Laboratories, Saikon, Koriyama, Fukushima 963-8862, Japan

12:50 **O-NDI-2** SECONDARY ELECTROSPRAY IONIZATION WITH ELECTRODELESS FOCUSSING: A NEW TOOL FOR METABOLOMIC KINETIC STUDIES

Guillermo Vidal-de-Miguel[(1)], Miriam Macia[(1)], José M. Vadillo[(2)]
[(1)] Fossil Ion Technology (FIT), Madrid, Spain; [(2)] UMA-LASERLAB, C/ Jimenez Fraud 4, 29071 Málaga, Spain

13:10 **O-OT-1** UNTARGETED METABOLOMICS AND LIPIDOMICS STRATEGIES BASED ON LIQUID CHROMATOGRAPHY HIGH-RESOLUTION MASS SPECTROMETRY: ARE YOU REALLY DRINKING TRADITIONAL PDO VALENCIA "ORXATA"?

Josep Rubert[(1,2,3)], Kamila Hurkova[(1)], Andoni Monforte[(4)], Jesús Blesa[(2)], José Luis Navarro[(3)], Gaspar Pérez[(3)], José Miguel Soriano[(2)], Jana Hajslova[(1)]
[(1)] University of Chemistry and Technology, Prague, Department of Food Analysis and Nutrition Technická 3, 166 28, Prague 6, Prague, Czech Republic; [(2)] Departament de Medicina Preventiva i Salut Pública, Facultat de Farmàcia, Universitat de València, 46100, Burjassot, Spain; [(3)] CSIC - Instituto de Agroquimica y Tecnologia de los Alimentos (IATA), Avda Agustín Escardino 7, Paterna, Valencia, Spain; [(4)] MonOrxata S.L., Carrer Picapedrers, 10, 46120 Alboraia, Valencia, España

13:30 **Lunch & Lunch Seminar (Bruker Daltonics)**

15:00 **Poster Session 4:** (detail in page 37)
Fundamentals and Chemometrics (FCH)
Isotopic analysis (IA)
Other Applications (OA)

15:50 Poster Flash Session 2:
Environmental Analysis (ENV)
Isotopic Analysis (IA)
Sample Preparation (SP)
Fundamentals and Chemometrics (FCH)
Other Applications (OA)

Session chairs: Belén Gómara Moreno – *IQOG-CSIC, Madrid*
Ana R. Díaz Marrero – *IUBO, University of La Laguna*

15:50 P-ENV-5 ASSESSING PALEOCLIMATIC CHANGES ARCHIVED IN SPELEOTHEMS FROM VOLCANIC CAVES BY PYROLYSIS GAS CHROMATOGRAPHY-BASED ANALYSES

Ana Z. Miller[(1)], José M. De la Rosa[(1)], Nicasio T. Jiménez-Morillo[(1)], Manuel F.C. Pereira[(2)], José A González-Pérez[(1)], Cesareo Saiz-Jimenez[(1)]
[(1)] Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC), Seville, Spain; [(2)] CERENA, Instituto Superior Técnico, Universidade de Lisboa, Lisbon, Portugal

15:55 P-ENV-21 PHOTODEGRADATION OF UV FILTERS IN THE AQUATIC ENVIRONMENT BY ADVANCED OXIDATION PROCESSES FOLLOWED BY SOLID-PHASE MICROEXTRACTION-GAS CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY

María Celeiro[(1)], Marlene Vila[(1)], Fabiola Vignola-Hackbarth[(2)], Vitor J.P. Vilar[(2)], María Llompart[(1)]
[(1)] Laboratory of Research and Development of Analytical Solutions (LIDSA). Department of Analytical Chemistry, Nutrition and Food Science. Faculty of Chemistry. University of Santiago de Compostela, E-15782, Santiago de Compostela, Spain; [(2)] Laboratory of Separation and Reaction Engineering-Laboratory of Catalysis and Materials (LSRE-LCM), Faculty of Engineering, University of Porto, 4200-465, Porto, Portugal

16:00 P-IA-4 EVALUATION OF UNCERTAINTY SOURCES IN THE DETERMINATION OF TESTOSTERONE IN URINE BY CALIBRATION-BASED AND ISOTOPE DILUTION QUANTIFICATION METHODS USING UHPLC-MS/MS

Jorge Pitarch-Motellón[(1)], Juan V. Sancho[(1)], María Ibáñez[(1)], Oscar Pozo[(2)], Antoni Francesc Roig-Navarro[(1)]
[(1)] Research Institute for Pesticides and Water, Universitat Jaume I, E-12071, Castellón, Spain; [(2)] Bioanalysis Research Group, IMIM, Hospital del Mar, 08003 Barcelona, Spain

16:05 P-SP-8 MAGNETIC HYPERCROSSLINKED PARTICLES TO EXTRACT SWEETENERS FROM ENVIRONMENTAL SAMPLES

Sameer S. Lakade[(1)], Qing Zhou[(2)], Francesc Borrull[(1)], Núria Fontanals[(1)], Rosa M. Marcé[(1)]
[(1)] Department of Analytical Chemistry and Organic Chemistry, Universitat Rovira I Virgili, Sescelades Campus, Marcel·lí Domingo s/n, Tarragona 43007, Spain; [(2)] State Key Laboratory of Pollution Control and Resources Reuse, School of the Environment, Nanjing University, Nanjing 210046, PR China

16:10 P-FCH-2 APPLICATION OF A CHIRAL SEPARATION TO EVALUATE THE RACEMIZATION PROCESS OF ATROPINE IN STRAMONIUM SEEDS: INFLUENCE OF pH AND TEMPERATURE

Jesús Marín-Sáez, Roberto Romero González, Irene Domínguez, Ana Romera Torres, Antonia Garrido Frenich
University of Almería, Department of Chemistry and Physics, Research Centre for Agricultural and Food Biotechnology (BITAL), Agrifood Campus of International Excellence ceiA3, Carretera de Sacramento s/n, E-04120 Almería, Spain

16:15 **P-OA-5** ASSESSMENT OF PESTICIDE RESIDUE EXTRACTION IN HONEY AND HONEYBEES

Pau Calatayud-Vernich[(1)], Fernando Calatayud[(2)], Enrique Simó[(2)], Yolanda Picó[(1)]
[(1)] Environmental and Food Safety Research Group, Desertification Research Centre (CIDE, UV-GV-CSIC), Faculty of Pharmacy, University of Valencia, Burjassot (Valencia), Spain; [(2)] Agrupación de Defensa Sanitaria Apícola apiADS, Ctra. Montroi-Turís, 46193 Montroi, Valencia, Spain

16:20 **Coffee Break & Exhibition**

16:40 **Young Scientists Session 2**

Session chairs: Begoña Jiménez Luque – *IQOG-CSIC, Madrid*
Marta Lores Aguín – *University of Santiago de Compostela*

16:40 **OJ-ENV-1** DETERMINATION OF PRIORITY AND OTHER HAZARDOUS SUBSTANCES IN RECYCLED RUBBER SPORT SURFACES BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY. STUDY OF THE ENVIRONMENTAL RISKS

María Celeiro[(1)], Carmen García-Jares[(1)], Thierry Dagnac[(2)], María Llompart[(1)]
[(1)] Laboratory of Research and Development of Analytical Solutions (LIDSA). Department of Analytical Chemistry, Nutrition and Food Science. Faculty of Chemistry. University of Santiago de Compostela, E-15782, Santiago de Compostela, Spain; [(2)] Galician Institute for Food Quality. Agronomic and Agrarian Research Centre (INGACAL-CIAM). Unit of Organic Contaminants, E-15080, A Coruña, Spain

16:50 **OJ-ENV-2** UHPLC-API-MS/MS *vs* GC-MS FOR THE DETERMINATION OF SEMIVOLATILE FLUORINATED ORGANIC COMPOUNDS

Juan Francisco Ayala Cabrera, Francisco Javier Santos Vicente, Encarnación Moyano Morcillo
Department of Chemical Engineering and Analytical Chemistry, University of Barcelona, Av. Diagonal 645, E-08028, Barcelona, Spain

17:00 **OJ-ENV-3** ULTRA-HIGH RESOLUTION MASS SPECTROMETRY (FT-ICR-MS): THE EFFECT OF A WILDFIRE IN SOIL ORGANIC MATTER

Nicasio T Jiménez-Morillo[(1)], Patrick G. Hatcher[(2)], Gonzalo Almendros[(3)], Francisco J. González-Vila[(1)], José A. González-Pérez[(1)]
[(1)] IRNAS-CSIC. Avda. Reina Mercedes 10, 41012, Sevilla, Spain; [(2)] Dept. of Chemistry and Biochemistry, Old Dominion University, Norfolk, Virginia, USA; [(3)] MNCN-CSIC. Serrano 115b, 28006, Madrid, Spain

17:10 **OJ-ENV-4** CONTRIBUTION OF FIREWORKS, FIRECRAKERS AND OPEN BURNING IN SPANISH POPULAR CELEBRATIONS TO CHLORINATED POPs IN AIR

Juan Muñoz-Arnanz, Belén González-Gaya, Jose Luis Roscales, María Ros, Alba Vicente, Begoña Jiménez
Department of Instrumental Analysis and Environmental Chemistry, Institute of Organic Chemistry (IQOG-CSIC). Juan de la Cierva 3, 28006 Madrid, Spain

17:20 **OJ-ENV-5** FORECASTING SOIL ORGANIC CARBON SEQUESTRATION BASED ON THE INCREASED COMPLEXITY OF PYROLYTIC METHOXYPHENOLS

Marco A. Jiménez-González[(1)], Gonzalo Almendros[(1)], Ana Álvarez[(2)], Francisco J. González-Vila[(3)]

[(1)] Museo Nacional de Ciencias Naturales (MNCN-CSIC), C/Serrano 115-B, Madrid, Spain; [(2)] Universidad Autónoma de Madrid (UAM), C/Francisco Tomás y Valiente 7, Madrid, Spain; [(3)] Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC), Av. Reina Mercedes 10, Sevilla (Spain)

17:30 **OJ-NDI-1** DETECTING ACIDIC PPCPs IN SEWAGE WATERS BY LIQUID CHROMATOGRAPHY HIGH RESOLUTION MASS SPECTROMETRY

Eric Carmona, María Jesús Andrés-Costa, Yolanda Picó

Environmental and Food Safety Research Group (SAMA-UV), Desertification Research Centre CIDE (CSIC-UV- GV), Faculty of Pharmacy, University of Valencia, Av. Vicent Andrés Estellés s/n, Burjassot, 46100 Valencia

17:40 **OJ-NDI-2** OVERCOMING MATRIX EFFECTS IN SMALL MOLECULE ANALYSIS BY LC-MS USING NANOFLOW LC AND HIGH DILUTION FACTORS

David Moreno-González, Antonio Molina-Díaz, Juan F- García-Reyes

Analytical Chemistry Research Group, Department of Physical and Analytical Chemistry, University of Jaén, 23071 Jaén, Spain

17:50 **OJ-SP-1** TRENDS IN ANALYSIS OF OXIDATIVE HAIR DYES

Eugenia Guerra, J. Pablo Lamas, María Llompart, Carmen García-Jares

Laboratory of Research and Development of Analytical Solutions (LIDSA), Department of Analytical Chemistry, Nutrition and Food Science, Faculty of Chemistry, Campus Vida, Universidade de Santiago de Compostela, E-15782 Santiago de Compostela, Spain

18:00 **OJ-SP-2** SIMPLE AND EFFECTIVE MULTIRESIDUE METHOD FOR 5-NITROIMIDAZOLE ANALYSIS IN FISH ROE SAMPLES BY UHPLC-MS/MS

Maykel Hernández-Mesa, Carmen Cruces-Blanco, Ana M. García-Campaña

Department of Analytical Chemistry, Faculty of Sciences, University of Granada, Campus Fuentenueva s/n, E-18071 Granada, Spain

18:10 **GENERAL ASSEMBLY OF SECyTA**

20:30 **Social Event**
Conference dinner at *Hacienda Montecarmelo*

Friday, November 4

08:30 Symposium Secretary Open

09:30 Oral Session 3: Clinical and Pharmaceutical Analysis (CPA)

Session chairs: José Manuel Florencio Nogueira – *University of Lisbon*
José María de la Rosa Arranz – *IRNAS-CSIC, Sevilla*

09:30 O-CPA-1 COMPREHENSIVE ANALYSIS TECHNIQUES OF EXTRACTABLES & LEACHABLES DETERMINATION IN PHARMACEUTICAL PRODUCTS
Jaume C. Morales[(1)], David A. Weil[(2)], Kevin Rowland[(3)], Mark Jordi[(3)]
[(1)] Agilent Technologies Spain S.L., WTC Moll de Barcelona, Spain; (2) Agilent Technologies Inc. Schaumburg, IL USA; [(3)] Jordi Labs Laboratory, 200 Gilbert St. Mansfield MA 02048 USA

09:50 O-CPA-2 DETERMINATION OF METHOTREXATE AND ITS MAIN METABOLITES BY LC-UHR-QTOF IN HUMAN SERUM OF LEUKEMIA PATIENTS WITH HIGH-DOSE ADMINISTRATION
Javier López
Laboratorio de Desarrollo de Aplicaciones Bruker Daltonics, Madrid, Spain

10:10 Coffee Break & Exhibition

10:30 Oral Session 4: Sample Preparation (SP)

Session chairs: José Luis Gómez Ariza – *University of Huelva*
Gonzalo Almendros Martín – *MNCN-CSIC, Madrid*

10:30 O-SP-1 DESIGNING NEW MICROEXTRACTION DEVICES FOR A BETTER USER-FRIENDLY ANALYTICAL APPROACH
J.M.F. Nogueira
Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal

10:50 O-SP-2 SYNTHESIS AND CHARACTERIZATION OF MAGNETIC COMPOSITES BASED ON MOFs INTENDED FOR MAGNETIC DISPERSIVE MICROEXTRACTION APPLICATIONS
Priscilla Rocío-Bautista[(1)], Verónica Pino[(1)], Jorge Pasán[(2)], Juan H. Ayala[(1)], Catalina Ruíz-Pérez[(2)], Ana M. Afonso[(1)]
[(1)] Departamento de Química (Unidad Departamental de Química Analítica), Universidad de La Laguna (ULL), 38206, La Laguna, Spain; [(2)] Grupo de Rayos X y Materiales Moleculares (MATMOL), Departamento de Física, Universidad de La Laguna (ULL), 38206, La Laguna, Spain

11:10 **O-SP-3** MIXTURE OF ANIONIC AND CATIONIC EXCHANGE SORBENTS TO SIMULTANEOUSLY EXTRACT ACIDIC ANB BASIC PHARMACEUTICALS FROM ENVIRONMENTAL WATERS

Núria Fontanals, Daniela Salas, Francesc Borrull, Rosa María Marcé
Department of Analytical Chemistry and Organic Chemistry, Faculty of Chemistry, Universitat Rovira i Virgili, Marcel.lí Domingo s/n, 43007, Tarragona, Spain

11:30 **O-SP-4** SCREENING OF SYNTHETIC CANNABINOIDS IN ORAL FLUIDS BY BAR ADSORPTIVE MICROEXTRACTION

S.M. Ahmad, N.R. Neng, H.M. Gaspar, J.M.F. Nogueira
Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal

11:50 **Closing Plenary Lecture**

Session chairs: Francisco Javier Santos – *University of Barcelona*
Francisco Javier González Vila – *IRNAS-CSIC, Sevilla*

11:50 **PL-5** ADVANCES IN ENVIRONMENTAL CHEMISTRY LINKED TO SEPARATION TECHNIQUES DEVELOPMENT: MY PERSONAL EXPERIENCE

María José González
Instrumental Analysis and Environmental Chemistry Department (AIQA), General Organic Chemistry Institute (CSIC). Juan de la Cierva 3, 28006-Madrid, Spain

12:30 **SECyTA2016 Closing Ceremony**

Francisco Javier Santos Vicente – President of SECyTA
University of Barcelona
José Antonio González Pérez – Chairman
IRNAS-CSIC, Sevilla
José Mª de la Rosa Arranz – Co-Chairman
IRNAS-CSIC, Sevilla
Francisco Javier González Vila – Scientific Committee Chairman
IRNAS-CSIC, Sevilla

Announcement of the José Antonio García Dominguez's Awards

Closing remarks

13:00 **Farewell Cocktail**

14:00 **Lunch Seminar (Frontier Lab)**

POSTER SESSIONS

Wednesday November 2

Poster Session 1:
Food Analysis (FA)

P-FA-1 VACUUM-HEADSPACE SOLID-PHASE MICROEXTRACTION FOR THE DETERMINATION OF FREE FATTY ACIDS AND PHENOLS IN MILK AND MILK DERIVATIVES
María J. Trujillo-Rodríguez, Verónica Pino, Elefteria Psillakis, Jared L. Anderson, Juan H. Ayala, Ana M. Afonso

P-FA-2 POLYMER-BASED MATERIALS MODIFIED WITH MAGNETITE NANOPARTICLES FOR ENRICHMENT OF PHOSPHOLIPIDS
Isabel Ten Doménech, José Manuel Herrero Martínez, Sagrario Torres-Cartas, Susana Meseguer-Lloret, Ernesto F. Simó Alfonso

P-FA-3 DEVELOPMENT OF MOLECULARLY IMPRINTED POLYMERS FOR SOLID-PHASE EXTRACTION OF PHOSPHOLIPIDS IN HUMAN MILK SAMPLES
Isabel Ten Doménech, José Manuel Herrero Martínez, Ernesto F. Simó Alfonso

P-FA-4 GC-MS AND HPAEC-PAD CHARACTERIZATION OF PECTIC OLIGOSACCHARIDES (POS) DERIVED FROM HYDROLYSIS OF CITRUS AND APPLE PECTINS
Carlos Sabater, Álvaro Ferreira, Laura Ruíz-Aceituno, Agustín Olano, Antonia Montilla, Nieves Corzo

P-FA-5 COMPARATIVE STUDY OF ANIONIC COMPOUNDS FOUND IN NATURAL AND PROCESSED JUICES ANALYZED BY CE-MS
Mª Paz Lorenzo, Loreto Muñoz, Ángeles López-Gonzálvez

P-FA-6 CHARACTERIZATION OF TMS DERIVATIVES OF GLYCOSYL-INOSITOLS BY GC-MS
Laura Ruiz-Aceituno, Cipriano Carrero-Carralero, Ana Isabel Ruiz-Matute, F. Javier Moreno Andújar, Isabel Martínez-Castro, María Luz Sanz

P-FA-7 DETERMINATION OF CURCUMIN AND RELATED COMPOUNDS BY HPLC-UV. APPLICATION TO THE CHARACTERIZATION AND AUTHENTICATION IN TURMERIC PRODUCTS
Concepción Domingo, Nuria Aliaga-Alcalde, Nuria Portolés-Gil, Javier Saurina

P-FA-8 CHARACTERIZATION AND CLASSIFICATION OF SPARKLING WINES BY LIQUID CHROMATOGRAPHY AND CHEMOMETRIC METHODS FOR DATA ANALYSIS
Anaïs Izquierdo, Sandrine Lucas Allée, Javier Saurina

P-FA-9 MONITORING THE VOLATILE PROFILE OF EXTRA VIRGIN OLIVE OILS FROM PICUAL AND HOJIBLANCA VARIETIES GROWN UNDER THREE CONDITIONS: CONVENTIONAL IRRIGATION, DRY FARMING AND ORGANIC PRODUCTION
Clemente Ortiz-Romero, Francisco Camacho, Rocío Ríos-Reina, M. Lourdes Morales, Brígida Jiménez, Raquel M. Callejón

P-FA-10 COMPARATIVE ASSESSMENT OF SOFTWARE FOR NON-TARGETED DATA ANALYSIS IN THE STUDY OF THE VOLATILE FINGERPRINT CHANGES DURING STORAGE OF A STRAWBERRY BEVERAGE
M. Lourdes Morales, Raquel M. Callejón, José L. Ordoñez, Ana M. Troncoso, Carmen García-Parrilla

P-FA-11 ANALYSIS OF DITHIANON BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY COUPLED TO TRIPLE CUADRUPOLE TANDEM MASS SPECTROMETRY
Marina López García, Roberto Romero González, Ana Romera Torres, Jesús Marín-Sáez, Antonia Garrido Frenich

P-FA-12 INFLUENCE OF OLIVE WASHING ON THE VOLATILE PROFILE OF AN ORGANIC EXTRA VIRGIN OLIVE OIL
Rocío Ríos-Reina, Clemente Ortiz-Romero, M. Lourdes Morales, Antonio J. Puentes, Pedro Vallesquino, Brígida Jiménez, Raquel M. Callejón

P-FA-13 A COMPARATIVE STUDY OF THE VOLATILE PROFILE OF WINE VINEGARS WITH PROTECTED DESIGNATION OF ORIGIN BY SORPTIVE EXTRACTION TECHNIQUES
Rocío Ríos-Reina, M. Lourdes Morales, José M. Amigo, Diego L. García-González, Raquel M. Callejón

P-FA-14 A SENSITIVE, QUANTITATIVE ANALYSIS OF MINOR COMPONENTS IN DEODORIZATION DISTILLATES OF VEGETABLE OILS
Miguel Martínez Quesada, Joaquín Velasco, M. Victoria Ruiz-Méndez

P-FA-15 STUDY OF CLEAN PROCEDURES TO APPLY QuEChERS TO DETERMINE PESTICIDE RESIDUES IN COFFEE LEAVES
María Teresa Salles Trevisan, Pau Calatayud, Ana Masiá, Yolanda Picó

P-FA-16 DETERMINATION OF ESTROGENIC COMPOUNDS IN MILK AND YOGURT SAMPLES BY HOLLOW-FIBER LIQUID-PHASE MICROEXTRACTION-GAS CHROMATOGRAPHY-TRIPLE QUADRUPOLE MASS SPECTROMETRY
Giovanni D'Orazio, Javier Hernández-Borges, Antonio Vicente Herrera-Herrera, Salvatore Fanali, Miguel Ángel Rodríguez-Delgado

P-FA-17 PRESENCE OF PLASTICISERS AND PRESERVATIVES IN DAIRY PRODUCTS BY UHPLC-ESI-QqQ(MRM). INFLUENCE OF STORAGE AND PACKAGING
Laura Herrero, Jesús E. Quintanilla, Mario A. Fernández, María José González, Belén Gómara

P-FA-18 ANALYSIS OF SEED OILS STEROLS AND FATTY ACID COMPOSITION BY METHYLATION AND COMBINATION OF CHROMATOGRAPHIC TECHNIQUES
Aída García González, Joaquín Velasco Jiménez, Leonardo Velasco Varo, M. Victoria Ruiz-Méndez

P-FA-19 DETERMINATION OF AROMATIC POLYCYCLIC HYDROCARBONS METABOLITES IN MILK SAMPLES, USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-FAST SCANNING FLUORIMETRIC DETECTION
Isabel Durán Martín-Merás, Álvaro Luque Uría, Anunciación Espinosa Mansilla

P-FA-20 PROFILING FOOD VOLATILES BY DIRECT COUPLING OF THERMAL DESORPTION AND MASS SPECTROMETRY. DIFFERENTIATION OF THYME CHEMOTYPES
Jesús Eduardo Quintanilla-López, Ana Cristina Soria, Rosa Lebrón-Aguilar

P-FA-21 PHOTOCHEMICAL STUDIES OF UV IRRADIATION OF FOLATES. POS-COLUMN ON-LINE PHOTODERIVATION FOR THE DETERMINATION OF FOLIC ACID AND ITS METABOLITES
Elísabet Martín Tornero, Isabel Durán Martín-Merás, Anunciación Espinosa Mansilla

P-FA-22 EVALUATION OF ENDOCRINE DISRUPTING PLASTICISER MIGRATION IN HOUSEHOLD FOOD CONTAINERS
Jorge Sáiz, Belén Gómara

P-FA-23 AUTHENTIFICATION OF IBERIAN HAM USING VOLATILE COMPOUNDS BY HEADSPACE-GAS CHROMATOGRAPHY-ION MOBILITY SPECTROMETRY
Natividad Jurado-Campos, Andrés Martín-Gómez, Natalia Arroyo-Manzanares, Rocío Garrido-Delgado, Cristina Arce, Lourdes Arce

P-FA-24 A COMPENDIUM OF FOOD AND BEVERAGE COMPARISONS WITH A NOVEL BENCHTOP GC-TOFMS SYSTEM
Lorne M. Fell, Elizabeth M. Humston-Fulmer, Joseph E. Binkley, Christina N. Kelly, Jonathan D. Byer, David E. Alonso

P-FA-25 MONITORING CARBOHYDRATE PROFILES OF COCOA BEAN FERMENTATION
Roberto Megias-Perez, Sergio Grimbs, Roy N. D'Souza, Warren A. John, Gino Vrancken, Matthias Ullrich, Nikolai Kuhnert.

P-FA-26 PECTIN ANALYSIS BY HIGH-PERFORMANCE SIZE-EXCLUSION CHROMATOGRAPHY USING EVAPORATIVE LIGHT SCATTERING DETECTION (HP-SEC-ELSD)
Nerea Muñoz-Almagro, Ana Muñoz, Mar Villamiel, Antonia Montilla

P-FA-27 USE OF ONION EXTRACT AS DAIRY CATTLE FEED SUPPLEMENT: MONITORING OF PTSO AS MARKER OF ITS EFFECT ON MILK ATTRIBUTES
Paloma Abad, Natalia Arroyo-Manzanares, Ana M. García-Campaña

P-FA-28 METHOD DEVELOPMENT FOR ERGOT ALKALOIDS IN CEREAL SAMPLES
Víctor Arrufat, Josep Lliberia Blasco, Jordi Díaz-Ferrero, Francesc Broto-Puig

P-FA-29 STUDY OF VOLATILE ORGANIC COMPOUNDS IN HYDROALCOHOLIC SAMPLES BY SPME-GC-FID
Anna Julià Martínez, Judith Báguena Polo, Josep Lliberia Blasco, Jordi Díaz-Ferrero, Francesc Broto-Puig

P-FA-30 DETERMINATION OF AMINOGLYCOSIDES IN MILK AND MILK-BASED FUNCTIONAL FOODS BY HILIC-BASED UHPLC-MS/MS AND MOLECULARLY IMPRINTED POLYMER SOLID PHASE EXTRACTION
Ahmed Mohammed Hamed, David Moreno-González, Laura Gámiz-Gracia, Ana M. García-Campaña

P-FA-31 DETERMINATION OF ESTROGENIC COMPOUNDS IN DAIRY PRODUCTS USING THE QuEChERS METHOD COMBINED WITH ULTRA HIGH PERFORMANCE LIQUID CHROMATOGRAPHY TANDEM MASS SPECTROMETRY
Bárbara Socas-Rodríguez, Javier González-Sálamo, Javier Hernández-Borges, Miguel Ángel Rodríguez-Delgado

P-FA-32 EXTRACTION AND CHARACTERIZATION OF BIOACTIVE INOSITOLS FROM MUNG BEAN
Drashti Mansukhani, Laura Ruiz Aceituno, Ana Isabel Ruiz Matute, Isabel Martínez Castro, María Luz Sanz

P-FA-33 DEVELOPMENT OF A GREEN MICROWAVE-ASSISTED EXTRACTION METHOD TO OBTAIN MULTIFUNCTIONAL EXTRACTS OF MENTHA *SP.*
María Jesús García, Ana Cristina Soria, Jesús Palá, Silvia Díaz, María Luz Sanz

P-FA-34 CAPILLARY ZONE ELECTROPHORESIS COUPLED WITH QUADRUPOLE-TIME-OF-FLIGHT MASS SPECTROMETRY FOR THE DETERMINATION OF QUINOLONES AND TETRACYCLINES IN MILK SAMPLES
D. Moreno-González, A.M. Hamed, L. Gámiz-Gracia, A.M. García-Campaña, A. Molina-Díaz

P-FA-35 INFLUENCE OF PHENYLALANINE AND UREA APPLICATION AT TWO DOSES TO GRAPEVINE LEAVES ON GRAPE VOLATILE COMPOSITION
Rosario González-Santamaría, Javier Portu, Rosa López, Pilar Santamaría, Teresa Garde-Cerdán

P-FA-36 NANOFLOW LIQUID CHROMATOGRAPHY HIGH RESOLUTION MASS SPECTROMETRY FOR MULTI-RESIDUE ANALYSIS OF VETERINARY DRUGS IN FOOD SAMPLES OF ANIMAL ORIGIN
J. Alcántara-Durán, David Moreno-González, Antonio Molina-Díaz, Juan F. García-Reyes

P-FA-37 DEVELOPMENT OF A POLYMERIC SORBENT MODIFIED WITH GOLD NANOPARTICLES FOR SOLID PHASE EXTRACTION OF HUMAN MILK WHEY PROTEINS
Isabel Ten Doménech, Ernesto Francisco Simó Alfonso, José Manuel Herrero Martínez

Poster Session 2:
Clinical and Pharmaceutical Analysis (CPA),
Natural Products (NP) & Omics Techniques (OT)

Clinical and Pharmaceutical Analysis (CPA)

P-CPA-1 ANALYSIS OF PROSTATE SPECIFIC ANTIGEN (PSA) BY CAPILLARY ELECTROPHORESIS AND TWO-DIMENSIONAL GEL ELECTROPHORESIS. COMPARISON AND COMPLEMENTARITY
Noemi Farina-Gómez, Sílvia Barrabés, Angel Puerta, Esther Llop, Jose Carlos Diez-Masa, Antoinette Perry, Rafael de Llorens, Rosa Peracaula, Mercedes de Frutos

P-CPA-2 ANALYTICAL STRATEGIES TO INVESTIGATE NPS IN LEGAL HIGHS
M. Ibáñez, D. Fabregat-Safont, I. Fornís, M. Ventura, C. Gil, N. Calzada, J.V. Sancho, F. Hernández

P-CPA-3 IS DEPROTEINIZATION NECESSARY IN THE DETERMINATION OF HUMAN PLASMATIC STEROIDS BY GC/IT-MS/MS ANALYSIS?
Antonio Fermín Toribio-Delgado, Robles-Gil, Marcos Maynar-Mariño, Guillermo Olcina-Camacho, Juan. I Maynar-Mariño

P-CPA-4 COMPARISON OF CHROMATOGRAPHIC PROFILES FROM ELECTROCHEMICAL AND IN VITRO ASSAYS FOR THE ASSESSMENT OF DRUG METABOLISM
Laura Rodríguez-Cid, Sonia Sentellas, Javier Saurina

P-CPA-5 DEVELOPMENT OF SIMPLE ISOCRATIC HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY ANALYTICAL METHOD FOR DETERMINATION OF PHYTOSTEROLS AND CHOLESTEROL IN PARENTERAL LIPID EMULSIONS
Ana Novak, Mercè Gutiérrez Zamora, Josep Manel Llop Talaveron, Josep María Suñé Negre, Pilar Pérez Lozano, Encarna García Montoya, Montserrat Miñarro Carmona, Josep Ramón Ticó Grau

P-CPA-6 ANALYSIS OF BASIC DRUGS IN PHARMACEUTICAL FORMULATIONS USING LIQUID CHROMATOGRAPHY WITH WATER AND DETERGENT
Ester Peris-García, Samuel Carda-Broch, María Celia García-Álvarez-coque, María José Ruiz Ángel

P-CPA-7 DYNAMIC CHANGES IN THE COMPOSITION OF THE CENTRAL NERVOUS SYSTEM MYELIN. STUDY AT DIFFERENT ADULT AGES BY LIQUID CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY
Mercedes Pintado-Sierra, Ana Bribián, Isabel García-Álvarez, Eva María Medina-Rodríguez, Rosa Lebrón-Aguilar, Leoncio Garrido, Alfonso Fernández-Mayoralas, Fernando de Castro, Jesús Eduardo Quintanilla-López

P-CPA-8 A NEW LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY METHOD FOR SULFATIDES SCREENING BASED ON THE WRONG-WAY-ROUND ELECTROSPRAY IONIZATION EFFECT
Mercedes Pintado-Sierra, Isabel García-Álvarez, Ana Bribián, Eva María Medina-Rodríguez, Rosa Lebrón-Aguilar, Leoncio Garrido, Fernando de Castro, Alfonso Fernández-Mayoralas, Jesús Eduardo Quintanilla-López

P-CPA-9 STRATEGIES FOR THE DETECTION OF NEW BISGLUCURONIDE, DIGLUCURONIDES AND DICONJUGATED METABOLITES OF ANABOLIC ANDROGENIC STEROIDS
Argitxu Esquivel, Aristotelis Kotronoulas, Georgina Balcells, Jesús Joglar, Rosa Ventura

P-CPA-10 ENANTIOMERIC DETERMINATION OF THE ANTIUREMIC DRUG COLCHICINE BY ELECTROKINETIC CHROMATOGRAPHY WITH ANIONIC CYCLODEXTRINS
Nuria Menéndez-López, Jesús Valimaña-Traverso, María Castro-Puyana, María Ángeles García, María Luisa Marina

P-CPA-11 HIGH RESOLUTION MASS SPECTROMETRY FOR THE IDENTIFICATION OF IN-VIVO 5-MeO-MiPT METABOLITES IN MOUSE SERUM AND URINE
D. Fabregat-Safont, M. Ibáñez, F. Martínez-García, C. Agustín-Pavón, A. Martín-Sánchez, J.V. Sancho, F. Hernández

Natural Products (NP)

P-NP-1 DIRECT DETECTION OF THE MONOTERPENE CARVACROL IN MAMMAL TISSUES BY ANALYTICAL PYROLYSIS (Py-GC/MS)
José A. González-Pérez, Francisco J. González-Vila, María Llana-Ruiz-Cabello, María Puerto, Silvia Pichardo, Ana M. Cameán

P-NP-2 CHROMATOGRAPHIC PROFILING OF *Camellia spp.* SEEDS COMPOSITION
Marta Lores, Marta Sánchez-Nande, Juan Pablo Lamas, Carmen García-Jares

P-NP-3 PRESSURIZED LIQUID EXTRACTS OF *Cytisus scoparius* SELECTIVELY-ENRICHED IN POLYPHENOLS
Marta Lores, Juan Pablo Lamas, C. García-Jares

Omics Techniques (OT)

P-OT-1 UHPLC-QTOF MS METABOLOMICS FOR BIOMARKER DISCOVERY IN NEURODEGENERATIVE DISEASES: ALZHEIMER AND CADASIL
Rubén Gil, Leticia Lacalle, Marlene Jiménez del Río, Carlos Alberto Vélez Pardo, Francisco Javier Lopera Restrepo, Félix Hernández Hernández, Juan Vicente Sancho

P-OT-2 ORGANOLEPTIC CHARACTERIZATION OF VIRGIN OLIVE OIL BY HS-GC-MS
Macarena Menéndez, Fernando Lafont, Isabel Mª García

P-OT-3 METABOLOMIC ANALYSIS OF SCROBICULARIA PLANA BY ORGANIC MASS SPECTROMETRY TO EVALUATE THE ENVIRONMENTAL STRESS
Gema Rodríguez Moro, Tamara García Barrera, Julián Blasco Moreno, José Luis Gómez Ariza

P-OT-4 STUDY OF METALS INTERACTIONS AND METABOLIC CHANGES CAUSED BY CADMIUM EXPOSURE OF MOUSE MUS MUSCULUS. PROTECTIVE EFFECT OF SELENIUM.
Mª del Rocío Baya-Arenas, Gema Rodríguez-Moro, Tamara García-Barrera, José Luis Gómez-Ariza

P-OT-5 TARGETED METABOLIC PROFILING OF PHENOLIC COMPOUNDS IN STRAWBERRIES UNDER DIFFERENT POST-HARVEST CONTROLLED ATMOSPHERE TREATMENTS
Sara Ramírez-Acosta, Ana Arias-Borrego, Tamara García-Barrera, José Luis Gómez-Ariza

P-OT-6 COMBINATION OF GAS CHROMATOGRAPHY-MASS SPECTROMETRY FOR METABOLOMIC STUDIES OF INFLAMMATORY DISEASES
A. Rodríguez-Fernández, T. García-Barrera, E. Talero, V. Motilva-Sánchez, J.L. Gómez Ariza

P-OT-7 INVESTIGATION OF LUNG CANCER BIOMARKERS IN HUMAN BIOLOGICAL FLUIDS BY METABOLOMICS BASED ON GAS CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY
Belén Callejón-Leblic, Tamara García-Barrera, Jesús Grávalos-Guzmán, Antonio Pereira-Vega, José Luis Gómez-Ariza

P-OT-8 IN-SOURCE FRAGMENTATION FOR METABOLITE IDENTIFICATION IN CE-TOF-MS APPLIED TO THE CHARACTERIZATION OF PLASMA SAMPLES
Maricruz Mamani, Joanna Godzien, Ángeles López-Gonzálvez, Coral Barbas

P-OT-9 PREDICTION OF HUMAN METABOLIC CLEARANCE OF ROSEMARY DITERPENES BY UHPLC-TOF MS ANALYSIS OF METABOLITES IN HEPARG CELL CULTURE SAMPLES
Argyro Giannakopoulou, Konstantina Theochari, Alberto Valdés, Tanize Acunha, Alejandro Cifuentes, Carolina Simó, Virginia García-Cañas

P-OT-10 HIGH RESOLUTION MASS SPECTROMETRY IN THE IDENTIFICATION OF METABOLITES AND TRANSFORMATION PRODUCTS FROM ENROFLOXACIN IN THERMALLY TREATED MILK FROM MEDICATED COWS
Alexandra Junza, Javier Saurina, Cristina Minguillón, Dolores Barrón

P-OT-11 STUDY OF THE POLAR METABOLOME BY REVERSED-PHASE LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY. EVALUATION OF DIFFERENT SAMPLE PREPARATION METHODS FOR PLASMA PROFILING
Elena Sánchez-López, Antonio L. Crego, María Luisa Marina

P-OT-12 A CROSS-PLATFORM METABOLIC WORKFLOW FOR VOLUME-LIMITED TISSUE SAMPLES. APPLICATION TO THE MICE MODEL OF POLYCYSTIC KIDNEY DISEASE
Elena Sánchez-López, Antonio L. Crego, María Luisa Marina, Dorien J. Peters, Oleg A. Mayboroda

P-OT-13 STUDY OF SEVERITY IN FOOD ALLERGY LINKED TO RESPIRATORY ALLERGY THROUGH METABOLOMICS
David Obeso, Alma Villaseñor, Rosace Domenico, María Marta Escribese, Marina Pérez-Gordo, Marcela Santaolalla, Montse Fernández-Rivas, Carlos Blanco, Maribel Alvarado, Domingo Barber, Coral Barbas

Thursday November 3

Poster Session 3:
Environmental Analysis (ENV),
New Developments in Instrumentation (NDI) & Sample Preparation (SP)

Environmental Analysis (ENV)

P-ENV-1 DEVELOPMENT OF A DISPERSIVE LIQUID-LIQUID MICROEXTRACTION GC-MS/MS METHOD FOR THE DETERMINATION OF WATER FRAMEWORK DIRECTIVE PRIORITY POLLUTANTS IN WATER SAMPLES
Adrià Rubirola, Jordi Quintana, Maria Rosa Boleda, Maria Teresa Galceran

P-ENV-2 ASSESSMENT OF TOTAL AND AVAILABLE POLYCYCLIC AROMATIC HYDROCARBONS IN BIOCHARS
José M. de la Rosa, Lidia Contreras-Bernal, Jaime Villaverde-Capellán, Fernando Madrid, Marina Paneque, Heike Knicker

P-ENV-3 METHOD DEVELOPMENT FOR PERFLUORINATED (PFAC) AND PHTHALATE COMPOUNDS IN SEAWATER SAMPLES
Rafael Cuenca, Mireia Singla, Josep Lliberia Blasco, Jordi Díaz-Ferrero, Francesc Broto-Puig

P-ENV-4 LIQUID CHROMATOGRAPHY QUADRUPOLE TIME-OF-FLIGHT DETERMINATION OF FIVE DRUGS IN VEGETAL BIOTA FROM DOÑANA´S NATIONAL PARK
Sofía Barreales Suárez, Miguel Ángel Bello-López, M. Villar-Navarro, R. Fernández-Torres

P-ENV-5 ASSESSING PALEOCLIMATIC CHANGES ARCHIVED IN SPELEOTHEMS FROM VOLCANIC CAVES BY PYROLYSIS GAS CHROMATOGRAPHY-BASED ANALYSES
Ana Z. Miller, José M. De la Rosa, Nicasio T. Jiménez-Morillo, Manuel F.C. Pereira, José A González-Pérez, Cesareo Saiz-Jimenez

P-ENV-6 ATMOSPHERIC PRESSURE CHEMICAL IONIZATION–GAS CHROMATOGRAPHY FOR THE CHARACTERIZATION OF CHLORINATED PARAFFINS
Adrià Rubirola, Borja Garlito, Fco. Javier Santos, Encarnación Moyano, Tania Portolés, María Rosa Boleda, Juan Vicente Sancho, María Teresa Galceran

P-ENV-7 SIMULTANEOUS DETERMINATION BY HPLC OF PYRETHRINS AND PYRETHROIDS IN WATER AND SEDIMENT SAMPLES
Alexander Ccanccapa, Ana Masiá, Yolanda Picó

P-ENV-8 ANALYTICAL CAPABILITIES OF GAS CHROMATOGRAPHY COUPLED TO HIGH RESOLUTION MASS SPECTROMETRY FOR THE ULTRA TRACE DETERMINATION OF CONTAMINANTS IN SURFACE WATER
Irene Domínguez, F. Javier Arrebola, Roberto Romero-González, Antonio Nieto-García, José L. Martínez Vidal, Antonia Garrido Frenich

P-ENV-9 REMOVAL OF ORGANIC MICROPOLLUTANTS IN WASTEWATER TREATMENT SCHEMES
Agustina de la Cal, Ignacio Martín, Carlos Echevarria, Sandra Casas, María Rosa Boleda

P-ENV-10 MULTI-RESIDUE ANALYSIS OF 36 PRIORITY AND EMERGING POLLUTANTS IN MARINE ECHINODERMS (*Holothuria tubulosa*) BY LIQUID EXTRACTION FOLLOWED BY DISPERSIVE SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY–TANDEM MASS SPECTROMETRY ANALYSIS
Alberto Zafra-Gómez, Julia Martín, Felix Hidalgo, Alejandro Ibáñez-Yuste, Jose Luís Santos, Irene Aparicio, Esteban Alonso, Jose Luís Vílchez

P-ENV-11 DETERMINATION OF SELECTED PARABENS, BENZOPHENONES, TRICLOSAN AND TRICLOCARBAN IN AGRICULTURAL SOILS AFTER AND BEFORE TREATMENT WITH COMPOST FROM SEWAGE SLUDGE. A LIXIVIATION STUDY
Alberto Zafra-Gómez, Francisco Javier Camino Sanchez, Rocío Rodríguez-Gómez, Jose Luís Vílchez

P-ENV-12 DEVELOPMENT OF METHODOLOGIES FOR THE QUANTIFICATION OF URINARY METABOLITES OF ORGANOPHOSPHATE AND PYRETHROID PESTICIDES AND ITS APPLICATION IN AGRICULTURAL POPULATIONS FROM CATALONIA AND GALICIA
Mercè Garí, Yolanda González, Joan O. Grimalt

P-ENV-13 LC-MS/MS AND HRMS ANALYSIS OF ESTROGENS INCLUDED IN WFD
Ane Iruretagoiena, Óscar Palacios, Cintia Flores, Francisco Javier Santos, Josep Caixach

P-ENV-14 COMPARATIVE OF TWO EXTRACTION TECHNIQUES OF MICROCYSTINS IN SEDIMENT: ACCELARATED SOLVENT EXTRACTION/ULTRASOUNDS
Laura Larrad, María Peg, Ana María Alonso, Manuel Toro

P-ENV-15 ARSENIC SPECIES BIOMONITORING IN URINE FROM ADULT POPULATION OF ANDALUSIA
F. Arellano-Beltrán, T. García-Barrera, B. González-Alzaga, I. López-Flores, I. Aroca-Siendones, M. Lacasaña, J. L. Gómez-Ariza

P-ENV-16 COMPARING CHROMATOGRAPHIC DATA FOR SOIL LIPID COMPOUNDS AS DENSITY SURFACES IN THE SPACE DEFINED BY THEIR ATOMIC RATIOS
Gonzalo Almendros, Pilar Tinoco, Sonia Rodríguez-Sánchez, Marco A. Jiménez-González, Jesús Sanz

P-ENV-17 DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN WATER SAMPLES BY USING MATERIALS CONTAINING BOUNDED CYCLODEXTRIN IN SOLID-PHASE EXTRACTION
Adela Mauri-Aucejo, Carolina Belenguer-Sapiña, Pedro Amorós, Alaina Moragues

P-ENV-18 COMPARATIVE EFFECTS OF SEVERAL CYCLODEXTRINS ON THE EXTRACTION OF POPs FROM CONTAMINATED SOILS AND SEDIMENTS
Esmeralda Morillo, Fernando Madrid, Rubén Ballesteros, Jaime Villaverde, Silvia Lacorte

P-ENV-19 PERSISTENCE OF SOIL ORGANIC MATTER AS A FUNCTION OF ITS MOLECULAR COMPOSITION AS REVEALED BY Py-GC/MS
Gonzalo Almendros, Zulimar Hernández, Jesús Sanz, Sonia Rodríguez-Sánchez, Marco A. Jiménez-González, José A González-Pérez

P-ENV-20 ANALYTICAL PYROLYSIS (Py-GC/MS) FOR RAPID MONITORING OF SOIL ORGANIC MATTER RECOVERY IN A CHRONOSEQUENCE OF SEMIARID MEDITERRANEAN BURNED FORESTS
Marco A. Jiménez-González, José M. De la Rosa, Nicasio T. Jiménez-Morillo, Gonzalo Almendros, José A. González-Pérez, Heike Knicker, Francisco J. González-Vila

P-ENV-21 PHOTODEGRADATION OF UV FILTERS IN THE AQUATIC ENVIRONMENT BY ADVANCED OXIDATION PROCESSES FOLLOWED BY SOLID-PHASE MICROEXTRACTION-GAS CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY
María Celeiro, Marlene Vila, Fabiola Vignola-Hackbarth, Vitor J.P. Vilar, María Llompart

P-ENV-22 A CHIRAL METHODOLOGY BY CD-MEKC TO STUDY THE TOXICITY OF BIOALLETHRIN ENANTIOMERS ON NON-TARGET ORGANISMS
Nuria Menéndez-López, Verónica Gil, María Castro-Puyana, Karina Boltes, María Ángeles García, María Luisa Marina

P-ENV-23 STUDY OF GEL PERMEATION CHROMATOGRAPHY TO PURIFY FOOD EXTRACTS FOR DETERMINATION OF PERSISTENT ORGANIC POLLUTANTS
Marta Riba Mirabet, Ramon Marti, Jordi Díaz-Ferrero

P-ENV-24 HOLLOW-FIBER LIQUID PHASE MICROEXTRACTION GAS CHROMATOGRAPHY TANDEM MASS SPECTROMETRY FOR THE DETERMINATION OF PHTHALATES IN WATER SAMPLES
Abenchara Betancor-Abreu, Javier González-Sálamo, Bárbara Socas-Rodríguez, Antonio V. Herrera-Herrera, Javier Hernández-Borges

P-ENV-25 COMPARATIVE STUDY OF THREE EXTRACTION METHODS FOR THE ANALYSIS OF ORGANOPHOSPHATE FLAME RETARDANTS IN SOIL AND BIOTA
María Lorenzo, Alba Pitarch, Yolanda Picó

P-ENV-26 ASSESSING DRUGS OF ABUSE DISTRIBUITON IN TURIA RIVER BASED ON GEOGRAPHIC INFORMATION SYSTEM AND LIQUID CHROMATOGRAPHY MASS SPECTROMETRY
María Jesús Andrés-Costa, Juan Antonio Pascual, Vicente Andreu, Yolanda Picó

P-ENV-27 THE EFFECT OF FIRE ON LIPID COMPOSITION OF SOIL SIZE FRACTIONS AND SOIL HYDROPHOBICITY
Nicasio T. Jiménez-Morillo, Jorge E. Spangenberg, José A. González-Pérez, Antonio Jordán, Lorena M. Zavala, Francisco J. González-Vila

P-ENV-28 QUANTITATIVE GC-MS ANALYSIS OF FREE LIPIDS FROM PINE AND JUNIPER LEAVES, LITTER AND SOILS
Cipriano Carrero-Carralero, Ana-Isabel Ruiz-Matute, Lourdes Ramos, Jesús Sanz, Gonzalo Almendros, María-Luz Sanz

P-ENV-29 DEVELOPMENT OF AIR SAMPLERS BASED ON CYCLODEXTRIN-SILICA COMPOSITES FOR ENVIRONMENTAL ANALYSIS
Carolina Belenguer-Sapiña, Adela Mauri-Aucejo, Pedro Amorós

P-ENV-30 STUDY OF SILICA-STRUCTURED MATERIALS FOR ORGANOPHOSPHORUS PESTICIDES SAMPLING AND DETERMINATION
Carolina Belenguer-Sapiña, Enric Pellicer-Castell, Adela Mauri-Aucejo, Pedro Amorós

P-ENV-31 ANALYTICAL PYROLYSIS (Py-GC/MS) OF SEDIMENTS: SEA-LEVEL RISE EPISODES DURING THE HOLOCENE IN THE POTENGI–JUNDIAI ESTUARY, NE BRAZIL
Mukesh Kumar, Tomasz Boski, Francisco P. Lima-Filho, Francisco H.R. Bezerra, Francisco J. González-Vila, José A. González-Pérez

New Developments in Instrumentation (NDI)

P-NDI-1 CHARACTERIZATION OF PLASMA PROFILES IN NEGATIVE IONIZATION MODE WITH DIFFERENT CAPILLARIES FOR CE-MS
Ángeles López-Gonzálvez, Vanesa Alonso-Herranz, Antonia García, Coral Barbas

P-NDI-2 SIMULTANEOUS DETERMINATION OF SEMIVOLATILE DBP IN DRINKING WATER SAMPLES BY LIQUID PHASE MICROEXTRACTION AND GAS CHROMATOGRAPHY-MS/μECD
A. Domínguez-Tello, A. Arias-Borrego, T. García-Barrera, J.L. Gómez-Ariza

P-NDI-3 NEW PYROLYSIS-GC/MS SYSTEM INCORPORATED WITH ON-LINE MICRO-UV IRRADIATION FOR RAPID EVALUATION OF PHOTO, THERMAL, AND OXIDATIVE DEGRADATION OF POLYMERS: STUDIES ON EPDM AND HIPS
Michael Soll, Akihiko Hosaka, Ichi Watanabe, Chu Watanabe

P-NDI-4 SCREENING OF PHENOLIC COMPOUNDS IN OLIVE FRUITS AND LEAVES BY HPLC-ESI-MS^n
Alicia Sánchez-García, Jose J. Ríos

P-NDI-5 CHIRAL SEPARATION OF NON-PROTEIN AMINO ACIDS BY ELECTROKINETIC CHROMATOGRAPHY. APPLICATION TO THE ANALYSIS OF FOOD SUPPLEMENTS
Raquel Pérez-Míguez, María Luisa Marina, María Castro-Puyana.

P-NDI-6 IMPLEMENTATION OF DIELECTRIC BARRIER DISCHARGE IONIZATION LC-MS SOURCE FOR FOOD, ENVIRONMENTAL AND BIOANALYTICAL APPLICATIONS
Rocío Nortes-Méndez, José Robles-Molina, Felipe J. Lara-Ortega, Antonio Molina-Díaz, Sebastian Brandt, Alexander Schütz, Joachim Franzke, Juan F. García-Reyes

Sample Preparation (SP)

P-SP-1 NEW GENERATION BAμE DEVICES FOR THE DETERMINATION OF TRIAZINIC HERBICIDES AND METABOLITES IN ENVIRONMENTAL WATER MATRICES
N.R. Neng, A.H. Ide, J.M.F. Nogueira

P-SP-2 DETERMINATION OF ANTIDEPRESSIVE COMPOUNDS IN REAL MATRICES BY NEW GENERATION BAμE DEVICES
A.H. Ide, S.M. Ahmad, N.R. Neng and J.M.F. Nogueira

P-SP-3 A GUANIDINIUM IONIC LIQUID-BASED SURFACTANT AS EXTRACTANT SOLVENT IN AN IN-SITU DISPERSIVE LIQUID-LIQUID MICROEXTRACTION METHOD FOR DETERMINING ENDOCRINE DISRUPTING POLLUTANTS
Idaira Pacheco-Fernández, Verónica Pino, Juan H. Ayala, Ana M. Afonso

P-SP-4 DETERMINATION OF PERFLUORINATED COMPOUNDS IN EDIBLE PLANT TISSUE BY LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY
Concepción Abril, Julia Martín, Juan Luis Santos, Irene Aparicio, Esteban Alonso

P-SP-5 OPTIMIZATION AND VALIDATION OF A METHODOLOGY TO QUANTIFY ENOLONES AND VANILLINES IN WINES BY AN AUTOMATED SOLID PHASE EXTRACTION FOLLOWED BY THEIR ANALYSIS THROUGH GAS CHROMATOGRAPHY-MASS SPECTROMETRY
Laura Culleré, Ernesto Franco-Luesma, Mónica Bueno, Julián Zapata, Vicente Ferreira

P-SP-6 DEVELOPMENT OF A MICROEXTRACTION METHOD USING A POLYMERIC SORBENT FOR TRACE ANALYSIS OF SELECTED PESTICIDES IN WATER SAMPLES
Ruben Vera, Clàudia Fontàs, Enriqueta Anticó

P-SP-7 ANALYSIS OF MULTI-CLASS SYNTHETIC WATER-SOLUBLE DYES IN COSMETIC AND FOOD SAMPLES BY MATRIX SOLID-PHASE DISPERSION AND LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY
Eugenia Guerra, María Llompart, Carmen García-Jares

P-SP-8 MAGNETIC HYPERCROSSLINKED PARTICLES TO EXTRACT SWEETENERS FROM ENVIRONMENTAL SAMPLES
Sameer S. Lakade, Qing Zhou, Francesc Borrull, Núria Fontanals, Rosa M. Marcé

P-SP-9 A GREEN AND EFFECTIVE METHOD FOR THE EXTRACTION OF ACIDIC PPCPs IN SEDIMENTS AND OTHER SOLID MATRICES
Eric Carmona, Vicente Andreu, Yolanda Picó

P-SP-10 URINE AS SOURCE OF PROSTATE CANCER BIOMARKERS. EFFECT OF SAMPLE PREPARATION ON CAPILLARY ELECTROPHORESIS OF PROSTATE SPECIFIC ANTIGEN
Noemi Farina-Gómez, Diana Navarro-Calderón, Angel Puerta, Manon Goasdoue, Eduardo Albers-Acosta, Carlos Olivier, José Carlos Díez-Masa, Mercedes de Frutos

Poster Session 4:
Fundamentals and Chemometrics (FCH),
Isotopic Analysis (IA) & Other Applications (OA)

Fundamentals and Chemometrics (FCH)

P-FCH-1 PIPETTE-TIP EXTRACTION OF PROTEINS USING A POLYMER MONOLITHIC PHASE MODIFIED WITH GOLD NANOPARTICLES
Oscar Mompó-Roselló, María Vergara-Barberán, José Manuel Herrero-Martínez, Ernesto F. Simó-Alfonso

P-FCH-2 APPLICATION OF A CHIRAL SEPARATION TO EVALUATE THE RACEMIZATION PROCESS OF ATROPINE IN STRAMONIUM SEEDS: INFLUENCE OF PH AND TEMPERATURE
Jesús Marín-Sáez, Roberto Romero González, Irene Domínguez, Ana Romera Torres, Antonia Garrido Frenich

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P-OA-8 A NOVEL BENCHTOP GC-TOFMS FOR FAST TARGETED ALLERGEN SCREENING AND NON-TARGETED CHARACTERIZATION FOR PERSONAL CARE PRODUCTS
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Tomás Herraiz, Andrea Flores

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Konstantina Theochari, Argyro Giannakopoulou, Tanize Acunha, Alberto Valdés, Alejandro Cifuentes, Carolina Simó, Virginia García-Cañas

ABSTRCATS

PL-1

UHPLC-MS-BASED METABOLOMICS STRATEGIES TO INVESTIGATE KNOWN AND NOVEL FUNGAL SECONDARY METABOLITES

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Fungi have the genetic machinery to produce many more secondary metabolites than are currently known. Ultrahigh performance liquid chromatography (UHPLC) hyphenated to high-resolution mass spectrometry (HRMS) is a very useful tool to explore the full capability of fungi in producing known and unknown metabolites. This is important in food safety research as well as for discovery of new bioactive compounds. The chemotype of fungal isolates is reflected by the production of a specific blend of mycotoxins and secondary metabolites and can be studied through an HRMS metabolomics approach. In this presentation this will be illustrated by research on ergot alkaloids and on secondary metabolite production by Aspergillus flavus (mainly known for production of aflatoxins), respectively.

Ergot alkaloids are mycotoxins produced by the Claviceps genus and they are frequently detected in cereals and cereal-based food. Commonly used analytical methods focus on 6 major compounds and their epimers. However class targeted metabolomics based on HRMS enabled an holistic determination of ergot alkaloids in rye samples and revealed an additional 19 ergot alkaloids, which could all be identified. While HRMS often focuses on qualitative analysis, the applied HRMS workflow allowed the quantitation of common ergot alkaloids and the identification of the unknowns in a single run.

HRMS and gene targeting was performed to explore secondary metabolites production by Aspergillus flavus. Fifty-five putative secondary metabolite gene clusters have been identified in A. flavus, but only for three of these biosynthetic genes, metabolites have been assigned. Very recently, the Laboratory of Food Analysis, Ghent University and that of USDA/ARS, New Orleans jointly discovered and elucidated the metabolites produced by four additional gene clusters (clusters 11, 23, 27 and 39), using HRMS and multiple stage MS (MSn)-based metabolomics.

This presentation will show that UHPLC hyphenated to HRMS and MSn are suitable tools in comparative metabolomics; allow rapid identification of known compounds and can be used to discover novel compounds and assign genes involved in biosynthesis of secondary fungal metabolites.

PL-2

EFFECTS OF WATER STRESS ON VINE LEAF SURFACE WAXES AND WINE VOCS: A GC-MS/FID AND GC-IRMS STUDY

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In the today's rapidly changing environment, plants are exposed to various abiotic stresses including more frequent and intense periods of water scarcity and drought. Grapevine (*Vitis vinifera*) is among the most expensive cultivated and sensitive crops, which often suffer from water stress. In water-stressed plants, the photosynthetic yield is low due to a decrease in both leaf area and photosynthetic rate per unit leaf area, causing different physiological and biochemical disorders. Variations in the chemistry, mobilization and deposition of extracellular lipids (epicuticular waxes) seem to module the response of plants to water stress [1]. In this work, we investigate the biogeochemical changes induced during development of field-grown cultivars of white (Chasselas) and red (Pinot noir) grapes (vineyards of Agroscope-IPV station, Valais, Switzerland) exposed to drought controlled by monitoring the soil water status and leaving all the other key environmental variables constant [2].

Among the initial field and laboratory measurements was the carbon isotopic composition (δ^{13}C values obtained by EA-IRMS) of the berry sugar at harvest (must sugar). The δ^{13}C values of must sugars (–27.6 to –22.5 ‰ VPDB) and leaf water potential during 10 growing seasons (2003 to 2012) were significantly correlated, indicating that these isotopic measurements allow a very sensitive detection of grapevine water status under natural conditions. These results motivated a study on possible similar chemical/isotopic response of (a) the vine leaf epicuticular waxes and (b) volatile organic compounds (VOCs) in the derived monovarietal wines produced from each grapevine variety using the same vinification protocol.

During 2014, leaves of Chasselas and Pinot Noir were collected monthly (n=120). Whole leaf tissues were analyzed for their carbon and nitrogen isotope composition (δ^{13}C and δ^{15}N values by EA-IRMS). GC-FID, GC-MS and compound specific carbon isotope analysis by GC-C-IRMS were used for analysis of acid and neutral lipids extracted from the leaf surfaces (n=21 Chasselas, n=21 Pinot Noir), and the VOCs in wines (n=36, vintages 2009-2014). For quantitation purposes and standardization of the δ^{13}C values, the samples were spiked before extraction with a standard mixture of compounds with known concentration and δ^{13}C values. The main results are distributions and δ^{13}C values of (a) *n*-alkanoic acids and *n*-alkanes from the leaf surface lipids (growing season 2014), and (b) >50 wine VOCs, among them, alcohols are the most abundant, followed by fatty acid esters, fatty and other carboxylic acids, ketones and other esters, lactones, aldehydes, amides and phenols. They will be discussed in terms of different cultivars, soil water status, growing season, and potential application as indicators of plant abiotic stress and wine terroir.

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PL-3

ANALYTICAL METHODS FOR THE STUDY OF HYDRAULIC FRACTURING FLUIDS

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State-of-the-Art analytical methods were used to analyze five different samples of hydraulic fracturing (HF) fluids. The methods include: ultrahigh performance liquid chromatography (UHPLC) coupled to quadrupole/time-of-flight mass spectrometry (QTOF-MS), time dispersive Ion-mobility mass spectrometry with accurate mass (IMS), and gas chromatography/gas chromatography with time-of-flight accurate mass (GCxGC/TOF). The HF fluids came from oil and gas wells from the Denver-Julesberg basin, which are part of a two-year study to determine the water chemistry and fate of chemicals used in the controversial and environmentally relevant topic of hydraulic fracturing. The purpose of this study was (1) to test the concept of " fingerprinting" the flowback and produced water from HF with drift time versus retention time (DT-RT) heatmaps using IMS, (2) to discover an unknown series of ethoxylated surfactants that were hidden in the complex mass spectra, (3) to apply collisional cross section (CCS) measurements to proton, sodium, and ammonium adducts to better understand the role that ion structure plays in fragmentation, (4) and to fingerprint the oil using heatmaps and GCxGC/TOF. Two new classes of ethoxylated surfactants were discovered by using DT-RT heatmaps combined with accurate mass and MS/MS analysis, as well as families of hydrocarbons, such as n-alkanes and aromatic hydrocarbons in the oil phase. The three analytical methods and their usefulness will be explained and discussed in detail, as well as the nature and chemistry of hydraulic fracturing fluids [1-2].

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PL-4

TANDEM OR HIGH RESOLUTION MASS SPECTROMETRY? THAT'S THE QUESTION IN ENVIRONMENTAL AND FOOD ANALYSIS

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In the last decades, one of the most important paradigms shift in environmental and food analysis arenas has been the shift from conventional detection systems in chromatographic techniques to couple gas chromatography (LC) and liquid chromatography (LC) to mass spectrometry. Mass spectrometry-based methods are nowadays the corner stones in the state-of-the-art of the instrumental techniques for the analysis of organic compounds in environmental and food sciences. In gas chromatography-mass spectrometry (GC-MS) single-stage MS is generally applied when electron ionization (EI) is used to identify compounds at low detection limits and to solve matrix interferences. Nevertheless, when chemical ionization techniques in GC-MS is required or when coupling liquid chromatography to mass spectrometry (LC-MS) using atmospheric pressure ionization sources (API), tandem mass spectrometry is necessary. Since the commercialization of triple quadrupole mass spectrometers in the 90s, the use of tandem MS has increased its popularity exponentially, thus allowing the development of analytical methods endowed with excellent sensitivity as well as with high selectivity, but offering important structural information useful for confirmatory purposes. This fact helped boost tandem MS to be the technique of choice for the determination of target compounds in many food and environmental laboratories.

Nowadays, the number of compounds to be analyzed simultaneously in environmental and food samples has increased drastically. In addition to the large number of new analytes, the range of compounds of interest has also expanded to include metabolites and transformation products, which show a wide variety of physicochemical properties. Additionally, sample treatments has been simplified to reduce analysis time and to be compatible with a wide range of family of compounds, thus improving throughput analysis in routine laboratories, but increasing the complexity of the final extracts. Additionally, the retrospective analysis of samples is more demanded to identify suspect compounds and unknowns. High-resolution mass spectrometry (HRMS) can deal with more of these new problems. HRMS has long been used in food and environmental analysis, although associated with high instrumental complexity, thus their use has been limited to the most demanding applications (natural organic matter or dioxin-related compounds). The development of modern HRMS instruments (time-of-flight (TOF) and Orbitrap) has fundamentally changed this situation. The new HRMS and hybrid MS/HRMS instruments are able to collect fast full scan spectra, with excellent mass accuracy, mass resolution, with no compound-related MS parameter optimization and there are suitable for quantitative analysis at very low concentration levels, but preserving maximum qualitative information. Consequently, the capabilities and limitations of current HRMS techniques in the field of food and environmental analysis must be reevaluated and we are foredoomed to a new paradigm shift in environmental and food anslysis.

PL-5

ADVANCES IN ENVIRONMENTAL CHEMISTRY LINKED TO SEPARATION TECHNIQUES DEVELOPMENT: MY PERSONAL EXPERIENCE

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The chromatography was born at the beginning of the 20th century when M.S. Tswett reported in 1901 as "chromatography" a new category of adsorption analysis in his first research work on the physico-chemical structure of plant chlorophylls. During more than 100 years there have been numerous and continuous advances in its development, to finally become the most widely used separation technique of the 21th Century.

The expression "technique" for referring to "chromatography" is not the most appropriate, because chromatography is more than a simple technique: it is an important part of science encompassing chemistry, physical chemistry, chemical engineering, biochemistry, and cutting through different fields such as environment, food technology, biology… In particular, the evolution of the chromatographic techniques, which went through a number of steps, has been decisive in the environmental chemistry development.

The focus of my research has been always the environmental chemistry field and, more precisely, the detection of toxic pollutants (either persistent or not) in several substrates. My working team was one of the pioneers in detecting persistent organic pollutants (POPs) not only in Spain but also internationally, since the early 1970s. My first studies in the 70's detecting the presence of organochlorine insecticides (DDTs, lindane, HCHs, HCB, etc.), methyl mercury and polychlorinated biphenyls (PCBs) in the environment were carried out thanks to one of the first commercially available GC-ECD devices (Model F11, Perkin Elmer) using a packed glass column (180 cm length x 0.18 cm i.d.) filled with a solid support covered by low polar stationary phase; an "in-line" injector and an ECD with high cell size volume. Later, my research was expanded into the analysis and characterization of environmental occurrence of both emerging contaminants (PCNs, toxaphenes, BFRs, PCTs, plasticizers, personal care products…) and more well-known contaminants, such dioxins, PAHs and chiral PCBs, in increasingly complex matrices (water, soil, biological matrices, food), at low concentrations (sub-ng level), which it has been possible thanks to the great revolution that we have witnessed in the separation techniques and the analytical instrumentation during the last 40 years.

During this lecture I will rather concentrate on a few selected relevant developments in separation techniques in the last 40 years and its impact on the results of my research in the fields of environmental chemistry and food security. Today, we are harvesting the results of those fundamental developments, often without any knowledge of the early achievement.

O-FA-1

DETERMINATION OF BISPHENOLS WITH ESTROGENIC ACTIVITY IN BABY FOOD SAMPLES BY SOLID-LIQUID EXTRACTION AND CLEAN-UP WITH DISPERSIVE SORBENTS FOLLOWED BY GAS CHROMATOGRAPHY TANDEM MASS SPECTROMETRY ANALYSIS

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Endocrine disrupting chemicals (EDCs) are a group of natural and synthetic chemicals that may interfere with the normal function of the endocrine system in animals and humans. Bisphenols (BPs) belong to this group of compounds [1, 2]. Bisphenol A (BPA), with an annual production of 2-3 million tons, is a fundamental building block in the synthesis of polycarbonate plastics and epoxy resins used in the production of a large variety of manufactured products. As health concerns over BPA in consumer products are increasing, this weak estrogen mimicking compound is gradually being replaced with structural analogs, whose environmental occurrence and estrogen risks are not well understood yet [3, 4].

In this work, a new sample preparation method for the determination of 7 BPs, with estrogenic activity, in baby food samples is presented. The procedure involves the extraction of the analytes from the sample using solid-liquid phase with acetonitrile followed by a further clean-up step with a mixture of dispersive-SPE sorbents, magnesium sulfate, C18 and PSA, in order to reduce matrix effects produced mainly produced by proteins, sugars or lipids. Extraction parameters were optimized using experimental design based optimization techniques. The compounds were detected and quantified by gas chromatography tandem mass spectrometry (GC–MS/MS). Analytes were separated in 11 min. Antracene was used as internal standard. The limits of quantification were between 0.2 and 0.4 ng g^{-1} for the studied analytes. The method was validated using matrix–matched calibration and recovery assays with spiked samples. Recovery rates were between 90% and 118% and % RSD was lower than 14% in all cases. The method has been successfully applied for the determination of these EDCs in a novel type of food samples consumed by preschoolers. This is the first time that these compounds are analyzed in packaged foods consumed by this population group.

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O-FA-2

BENEFITS OF USING MASS DETECTION FOR ROUTINE AMINO ACID ANALYSIS

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Quantitative measurements of amino acids are generally used for molecular diagnostics in heath science. For amino acid quantification, the current gold standard analytical method is somewhat lengthily (~3hours). With an ever increasing need to improve sample throughput, the challenge is to replace this well established method with an alternative approach.

This presentation shows a new analytical method with mass detection, that still allows simple sample preparation, but greatly reduces analysis time needed.

The analytical method is based on AccQ•Tag™ pre-column derivatisation followed by a rapid UPLC® separation using a simple mass detector for detection.

The obtained new analysis method shortens the overall analysis time significantly whilst maintaining robustness and reproducibility. Furthermore, this approach enables better resolution and sensitivity, hence simplifying some aspects of sample preparation and facilitating optimization of others.

O-FA-3

VALORIZATION OF BLACK CHOKEBERRIES (*Aronia melanocarpa*) POMACE AND CHEMICAL CHARACTERIZATION BY COMPREHENSIVE TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY

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This work shows a new alternative for the downstream processing and valorization of black chokeberry pomace (*Aronia melanocarpa*) which could be potentially coupled to a biorefinery process. Biorefinery relies on the development of integrated production processes in which all kinds of materials and by-products are converted in valuable end-products, including energy, biofuels and chemicals. This new procedure is based on the application of pressurized liquid extraction (PLE) to the residue obtained after the supercritical fluid extraction (SFE) of the berry pomace. The main aim is to produce a valorization of this important food-related by-product. An experimental design is employed to study and optimize the most relevant extraction conditions in order to attain extracts with high extraction yields, total phenols content and antioxidant activity.

Moreover, the obtained PLE extracts were characterized by using a new method based on the application of two-dimensional comprehensive liquid chromatography coupled to mass spectrometry (LC×LC-MS/MS) in order to correlate their activity with their chemical composition. A microbore amino column was used in the first dimension eluted at 18 µL min^{-1} coupled to a short partially-porous C18 column in the second dimension, using a flow rate of 3 mL min^{-1}. This approach provided with a good degree of orthogonality (as could be inferred from the peaks distribution obtained along the 2D plane, and high theoretical peak capacity, equal to 1693.

Thanks to the use of this powerful analytical tool, 61 compounds could be separated being possible the tentative identification of different anthocyanins, proanthocyanins, flavonoids and phenolic acids. By using the optimized PLE approach (using pressurized 46% ethanol in water at 165 ºC containing 1.8% formic acid), extracts with high total phenols content (236.6 mg GAE g^{-1} extract) and high antioxidant activities (4.35 mmol TE g^{-1} extract and EC_{50} 5.92 µg ml^{-1}) could be obtained with high yields (72.5%). Using those analytical conditions in combination with DAD and MS detectors, a good separation of the complex PLE extracts could be obtained

O-FA-4
DEVELOPMENT OF LC-MS/MS METHODS FOR THE SIMULTANEOUS QUANTIFICATION OF MYCOTOXINS IN MILK

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Mycotoxins are toxic secondary metabolites produced by fungal species that contaminate vegetal products. When ruminants are fed with contaminated feedstuffs, mycotoxins can be metabolized in the rumen or absorbed, reaching tissues and biological fluids such as milk. In addition, some metabolites, such as aflatoxin M1, which is produced in the liver metabolism of aflatoxin B1, can be carried over into milk. Mycotoxins can reach man through milk, affecting human health. The International Agency for Research on Cancer has classified aflatoxin B1 and naturally-occurring mixtures of aflatoxins as human carcinogens (group 1) and ochratoxin A as a possible human carcinogen (group 2B) [1]. Thus, analysis of mycotoxins in milk is necessary. The development and validation of methods capable of simultaneously detecting several mycotoxins are particularly relevant as ruminants are usually exposed to multiple mycotoxins due to the fact that their diet is prepared from different raw materials and in each one of them, contamination by different fungi species is likely. In the European Union, only the presence of aflatoxin M1 is regulated in milk with a maximum permitted level of 0.05 μg/kg [2].

In this study, the development and validation of two LC-MS/MS-based methods for the quantification of 22 mycotoxins in milk are presented. The 22 mycotoxins have been classified into two groups. Group A included the trichothecenes nivalenol, deoxynivalenol, deepoxy-deoxynivalenol, 3-acetyldeoxynivalenol, 15-acetyldeoxynivalenol, neosolaniol, diacetoxyscirpenol, fusarenon X, T-2 and HT-2. Group B included aflatoxins B1, B2, M1, G1 and G2, fumonisins B1, B2 and B3, ochratoxins A and B, zearalenone and sterigmatocystin. Sample treatment is simple in both cases and based on liquid-liquid extraction with acidified acetonitrile. After centrifugation and separation of the upper phase, water phase separation was induced by adding CH_3COONa. Each acetonitrile phase was dried and the residues were reconstituted with LC mobile phase. Mycotoxin group A was reconstituted with mobile phase at 5% of component B and group B with 40% B. The two groups of mycotoxins were analyzed by means of LC-MS/MS (ESI) in separate runs with different separation conditions. Validation of the methods has been based on the following parameters: limits of detection and quantification, linearity, accuracy, precision, recovery, stability and matrix effects. A detection limit of 0.025 μg/L was achieved for AFM1.

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O-NP-1

CHROMATOGRAPHIC METHODS FOR *NANNOCHLOROPSIS GADITANA* MICROALGAE EXTRACTS' PROFILING

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Microalgae are natural products that have gained a lot of attention in the last years as a feedstock for biorefinery. They are rich in bioactive compounds such as long chain polyunsaturated fatty acids (LC-PUFAs), carotenoids and proteins. The development of sustainable processes for the fractionation of natural products in biofuels plus ingredients for nutraceuticals, cosmetics or bioplastics is a hot topic of research nowadays.

In the present work, the extraction of bioactive compounds with antioxidant activity from *Nannochloropsis gaditana* has been investigated. High-pressure homogenization (HPH) was used to break down the strong cell wall. Supercritical fluid extraction (SFE) using pure CO_2 was performed based on previous reports available in the literature [1]. The remaining by-product was treated by pressurized liquid extraction (PLE). An experimental design based on response surface methodology (RSM) was proposed for the recovery of bioactive compounds by PLE using green solvents such as water and ethanol. Solvent composition and temperature were the independent factors.

Several chromatographic methods were used for the characterization of the obtained extracts, in an attempt to correlate the composition of the extracts with the antioxidant activity obtained. Reverse phase High-performance liquid chromatography with diode array detection (HPLC-DAD) was used for the characterization of pigments profile; normal phase HPLC with evaporative light scattering detection (HPLC-ELSD) was used for the study of lipids profile, and gas chromatography with mass spectrometry detection (GC-MS) was employed to determine the fatty acids profile. The present study points out the importance of chromatographic methods as essential analytical tools in the field of food science and natural products research.

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O-NP-2

PHLEBODIUM DECUMANUM: CHROMATOGRAPHIC CHARACTERIZATION OF A NATURAL EXTRACT

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Phlebodium decumanum and related tropical ferns grouped under the name **Calaguala** have been empirically used in Honduras and other Central and South American countries since ancient times to improve health in a variety of conditions related to inflammatory processes, dermatological disorders and even cancer. The first information about the benefits of these plants was provided by Hipólito Ruiz in 1805.

There are evidences of anti-neoplasic potential and anti-inflammatory, immunomodulatory and antioxidant properties of the extract. *In vitro* experiments revealed its anti-inflammatory properties based on the decrease of pro-inflammatory cytokines such as TNF-α and IL-6 in cultured macrophages. In addition, the extract increases the production of soluble TNF receptor 2 (sTNFR-2) that reduces the biological activity of this pro-inflammatory cytokine [1]. In addition to the immunomodulatory effects described above, antioxidant effects are also attributed, since individuals treated with the extract showed an increase in the serum concentrations of the two analyzed antioxidants (α-tocopherol and coenzyme Q_{10}). A decrease in the damage of mitochondrial DNA of T lymphocytes, damage that usually is associated with oxidative stress, was also seen in individuals treated. Other studies have focused on the effect of *P. decumanum* intake on fatigue and exhaustion [2].

Although these effects are of great interest for the treatment of infectious processes and organ deterioration that often accompanies tumors and their treatments, preliminary studies showed a direct antitumor activity of *P. decumanum* extracts. Specifically, the study by Gridling M *et al.* [3] reveals that extracts obtained from the fronds of *P. decumanum* inhibit the proliferation of the HL-60 tumor line (pro-myelocytic leukemia).

Now a days, the ignorance of compounds present in this specie, as well as of their potential properties, makes necessary a deeper study, beginning with the study of its chromatographic profile. In this context, the main issue of this work was the establishment of a chemical profile representative "fingerprint" of the different compounds that are extracted from the fern. The different variables and instrumental parameters that affect to the chromatographic separation were optimized. The stationary phase was selected and the composition of the mobile phase, the flow and the volume of injection optimized. During the development of this work, a UHPLC equipment was used.

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O-ENV-1

DETERMINATION OF HIGHLY POLAR PESTICIDES IN LETTUCE AND CELERY BY QUICK POLAR PESTICIDES EXTRACTION METHOD AND DIRECT ANALYSIS IN REAL TIME

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The determination of highly polar pesticides in food samples with high water content is a challenge that analytical chemists are currently facing. EU Reference laboratories have developed a fast and simple method for this purpose called Quick Polar Pesticides Extraction method (QuPPe) [1]. Unfortunately, sample extraction selectivity is poor as there is no partition stage. Furthermore, there are 12 different LC-MS/MS methods depending on the analyte suite required. This fact hinders its application in routine analysis laboratories. Direct analysis in real time (DART) is an ambient pressure desorption ionization technique, which uses a hot stream of metastable helium to both desorb the analytes from the matrix and ionize them so they can be detected by mass spectrometry [2]. Like the QuPPe method, the main advantage of DART is the speed of analysis. When combined with high resolution mass spectrometry (HRMS), it can achieve the required selectivity for identification of pesticides in food samples according to the current European legislation (SANTE/11945/2015). It is expected that an analytical method based on QuPPe-DART exhibits superior performance in terms of cost and speed of analysis, making it ideal as screening method.

In this work, we have developed and optimized a QuPPe-DART-HRMS for the determination of 7 highly polar pesticides in lettuce and celery. The QuPPe method was modified by adding an extra clean-up step using primary-secondary amine (PSA). Significant DART parameters such as desorption temperature, scanning speed and distance between the sample and the DART source were optimized. A comparison between Time-of-flight and Orbitrap mass spectrometers was carried out in terms of DART suitability. Finally, the quantitative potential of this method was assessed for the determination of amitrole, cyromazine, propamocarb, melamine, diethanolamine, triethanolamine and triazole in lettuce and celery samples. Good linearity ($R^2 \geq 0.999$) was achieved between 100 and 500 µg/kg with limits of detection between 16 and 56 µg/kg. Relative standard deviations were usually below 12% (no internal standard was used) and recoveries ranged between 71 and 115%. QuPPe-DART-HRMS is not just ideal as screening method but also shows potential for quantitation.

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O-ENV-2

UNAMBIGUOUSLY DICERNING HOST RANGE IN THE HOLOPARASITE *Cistanche phelypaea* (L.) (Orobanchaceae) USING PYROLYSIS-COMPOUND SPECIFIC ISOTOPE ANALYSIS (Py-CSIA)

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Carbon isotope composition is widely used to distinguish plants with major photosynthetic pathways. Most terrestrial plants are C3 plants with $\delta^{13}C$ values ranging from -24 to -34 ‰, whereas many aquatic, desert, salt marsh plants as well as tropical grasses have the dicarboxylic acid (C4) pathway and higher $\delta^{13}C$ values from -6 to -19 ‰ [1]. However within these groupings there is variation and other factors contribute to differences in $\delta^{13}C$ signatures i.e. environmental conditions and water use efficiency [2], plant parts and organs [3] and tissue ageing and decomposition [4]. Furthermore there is also $\delta^{13}C$ variation within specific plant compounds i.e. alkanes, lipids [5], cellulose and lignin [6].

Cistanche is a genus of plants with worldwide distribution with no photosystem that obtain nutrients and water from the host plants whose roots parasitize. All of its fixed carbon derives from the host plant. Bulk carbon isotope analysis has been used to detect hosts in obliged and facultative parasitic plants, however matching is not always as expected; in general it is known that $\delta^{13}C$ in parasitic plants tissue is slightly but consistently enriched as compared with the host by between 1.0 and 1.5 ‰ [7]. This difference provides a good chance for false matchings, especially when trying to assert host plants growing close together and mixed under the same environmental conditions, that also favours the occurrence of extensive and complex root systems i.e. wetlands or marshes [8].

The parasitic association between species and the obliged parasitic plant *Cistanche phelypaea* (L.) is studied in the Odiel Marshes Biosphere Reserve, Huelva, (SW Spain). The use of conventional carbon IRMS analysis of bulk lyophilized tissue was found of limited value to tie parasite and host plant. Pyrolysis compound specific carbon isotope analysis (Py-CSIA) of bulk lyophilized tissue was a very accurate technique in associating a particular parasite with its host. This study also unambiguously detected hosts of *C. phelypaea* and effectively demonstrating its ability to thrive on both C3 (*Arthrocnemum macrostachyum* (Moric.), *Limoniastrum monopetalum* (L.) Boiss. and *Halimione portulacoides* (L) Aellen) and C4 (*Atriplex halimus* L.) photosystem-type plants. Up to know no parasitism could be confirmed between *C. phelypaea* and the C4 photosystem-type species *Spartina densiflora* Brong. (C4) *Salsola sp.* (cf. *brevifolia*) although not discarded, research is still in progress.

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O-ENV-3

COMPREHENSIVE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN ATMOSPHERES THAT ARE UNDER INFLUENCE OF THE EMISSIONS FROM A CHLOR-ALKALI PLANT

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Chlor-alkali plants devoted to the synthesis of organochlorine solvents are known sources of hexachlorobenzene (HCB) and carbon tetrachloride to the atmosphere. Obviously, they may also release small amounts of the manufactured organochlorine solvents. However, no previous study has addressed the characterization of the whole mixture of organochlorine compounds emitted to the air by these installations. We have taken here as model a chlor-alkali plant located in Flix. Previous work in this area showed that large amounts of hexachlorobenzene (HCB) had been emitted to the nearby atmosphere in the past [1]. At present, removal of factory residues from the Ebro River released to the air a complex mixture of organochlorine compounds that has been analyzed by thermal-desorption gas-chromatography coupled to mass-spectrometry (TD-GC-MS). Besides the common organochlorine solvents synthesized in the factory, e.g. trichloroethylene and tetrachloroethylene, with levels ranging from 0.1 μg/m^3 to 140 μg/m^3, more than 50 other by-products have been identified. Several active sampling campaigns in more than ten sites nearby the factory were performed in 2013, 2014 and 2015, using different sorbents, such as Carbopack and Tenax. The results of the analysis showed important fluctuations of HCB concentrations among the different sites and sampling campaigns, although the concentrations were generally lower than those observed in the past [1]. Highest HCB levels coincided with detectable levels of hexachlorobutadiene, although the concentrations did not trespass exposure risks. The non-chlorine VOCs, such as benzene, toluene and xylenes, showed a different distribution pattern than the chlorinated VOCs which was related to local traffic emissions. The applied methodology allows the detection and quantification of a wide range of known and previously unknown VOCs in the atmosphere. The present study provides a reference case when addressing the possible impacts of this type of chlor-alkali plants to the environment.

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O-NDI-1

EXPANDING CAPABILITIES OF GC/MS SYSTEMS USING VERTICAL FURNACE PYROLYZER: DEFORMULATION AND IDENTIFICATION OF UNKNOWN POLYMERIC MATERIAL

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We have developed a vertical micro-furnace pyrolyzer utilizing a free-fall sample introduction mechanism along with various functions such as temperature programmable heating [1]. The vertical micro-furnace pyrolyzer combined with gas chromatography/mass spectrometry (GC/MS) system has become one of the most powerful analytical instruments in various fields such as the characterization of synthetic and natural polymers, art dyes and materials, archaeological artefacts, soil organic matter, biological samples and use in general forensic sciences and in the modelling of pyrolysis processes of biomass and plastic wastes.

A comprehensive approach to fully characterize and to identify unknown polymers in mixture or within complex matrices demands the use of an array of analytical techniques that provide complementary information. Evolved Gas Analysis (EGA-MS), Heart-cut EGA (EGA-GC/MS), Single/Multiple Shot Pyrolysis Analysis (PY-GC/MS) or Thermal Desorption Analysis (TD-GC/MS) are all appropriate techniques available from Frontier Lab and developed with in-house technology. These techniques produce fragments that represent the original material (markers) and that can be easily identified and associated to chemical structural information by comparison with stored data available in mass spectral libraries. F-Search is a database software specifically designed to characterize polymeric materials and additives from pyrograms and EGA thermograms. The core of F-Search is a patented search algorithm that together with specialized Frontier Lab. MS libraries, facilitates the characterization of polymers and additives.

In this work the system design of the Frontier Lab vertical furnace pyrolyzer is described and the four main analytical methods explained. Practical applications recently developed will also be presented that include the analysis of a complex sample from the cosmetic industry (de-formulation approach to characterize commercial eyeliners), automotive industry (wheaterability of EPDM), food industry (sugar fraud detection in combination with compound specific isotope analysis Py-CSIA) [2]) and from new food package industry trends (additives in polylactic acid based bio-plastics) [3].

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O-NDI-2

SECONDARY ELECTROSPRAY IONIZATION WITH ELECTRODELESS FOCUSSING: A NEW TOOL FOR METABOLOMIC KINETIC STUDIES.

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Secondary Electro-Spray Ionization (SESI) in tandem with High Resolution Mass Spectrometry (SESI-HRMS) is a very powerful tool for the analysis of volatile samples. Ions generated by an electrospray can transfer their charge to the polar vapors in contact with spray mist. One of the first applications of SESI was detecting explosives below the ppt level [1]. The technique has also been used for the analysis of breath, enabling for the detection of very low volatility species, which were previously rendered as non-volatile.

This has opened the field of metabolic analysis with rapid time resolution. Metabolites naturally released to the air steam in minute concentrations can be detected in real time, and non invasively. Despite its great combination of sensitivity and selectivity, SESI-HRMS analysis is still not an established technique. Here we describe the development of the first SESI source designed to meet the needs of this type of applications.

We studied the ionization mechanisms [2, 3]. The first optimized ionizers increased the flow of ions [4,5]. However, the optimized SESI required more electrodes and voltages to guide the ions. In practice, the robustness of the system was reduced, and background levels increased. Although the high ionization efficiencies achieved enabled for the detection of very low volatility species, they are more prone to adhere to the inner surfaces of the ionizer, specially in stagnated regions, and thus produce higher backgrounds

We have used a new numerical tool that combines finite element methods in the bulk domain and an analytical solution at the tip of the spray to overcome numerical instability problems associated with the electrospray tip. This has been instrumental to tackle our designs with an new level of detail.

Here we present a new configuration designed to maximize the transmission of ions into the MS, and to minimize background levels. This is accomplished by eliminating the electrodes that were previously used to guide the ions, and by carefully designing the flows of gases, and the electric fields generated by the electrospray so as to minimize dilution and maximize ion transmission. Sample ions are generated and pushed by the electric field produced by the spray, and then they are focused towards the MS inlet. By eliminating the electrodes, the contact area with the walls of the system is minimized, and stagnated regions are eliminated.

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O-OT-1

UNTARGETED METABOLOMICS AND LIPIDOMICS STRATEGIES BASED ON LIQUID CHROMATOGRAPHY HIGH-RESOLUTION MASS SPECTROMETRY: ARE YOU REALLY DRINKING TRADITIONAL PDO VALENCIA "ORXATA"?

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Food fulfils a basic need, consumed to provide nutritional support and energy for the body, as well as to stimulate growth and maintain life. A part from the nutritional aspects, consumers get a deep sense of satisfaction for genuine products. In this frame, tiger-nuts milk also called "Orxata", is a well-know product in Spain, especially in Valencian region, and represents a beverage that consumers are very willing to pay more for. In fact, consumers and local authorities have always demanded food quality and food safety, but today they also demand food authenticity. Hence, the availability of fast and simple authentication strategies in terms of the verification of label statements and nutritional aspects is currently highly required. In this research two steps can be distinguished: (i) raw material, origin verification based on tiger-nuts (xufa), and (ii) verification and comparison of nutritional aspects using traditional tiger-nuts milk (orxata) and UHT tiger-nuts milk beverages. On the one hand, fifty tiger-nut samples were initially provided by local producers and Protected Designation of Origin (PDO) "Xufa de Valencia". This sample set was explored by a Lipidomics approach in order classify samples according to their geographical origin. In the first phase, a solid liquid extraction procedure was optimized followed by liquid chromatography separation coupled with high-resolution mass spectrometry (UHPLC-HRMS), UHPLC-TripleTOF 6600. After data pre-treatment and data processing, lipidome revealed significant differences between PDO Valencian samples and unknown samples. On the other hand, eighty tiger-nuts milk samples; UHT (40) and traditional tiger-nuts beverages (40) were nicely compared in order to understand the impact of food processing on the nutritional quality. In this way, an untargeted metabolomics strategy was introduced based on UHPLC-HRMS, as a tool for monitoring the fingerprints of the beverage for the purpose of tracking its standard chemical pattern. Supervised and unsupervised statistical models showed up significant differences between UHT and traditional tiger-nuts milk related to free fatty acids, phospholipids and carbohydrate profiles. In parallel, vitamins, lipids, polyphenols, which have been already described in this beverage, were successfully monitored, and trend plots depicted major changes in some cases. Therefore, a twofold strategy based on food metabolomics, starting in the raw material and finishing in the end-product, contributed substantially to answer if we drink traditionally PDO"Orxata".

O-CPA-1

COMPREHENSIVE ANALYSIS TECHNIQUES OF EXTRACTABLES & LEACHABLES DETERMINATION IN PHARMACEUTICAL PRODUCTS

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Compounds leaching from container closure systems can cause contamination to drug substances or products. As part of a risk evaluation, it is necessary to identify these compounds and ensure that the drugs are suitable for their intended use.

The US Food and Drug Administration (FDA) has issued guidance on container closure systems for packaging human drugs and biologics [1], due to the potential risk that impurities pose to consumer health. The guidance document includes protection, safety, and compatibility guidelines. In general, profiling extractables and leachables (E&Ls) is a complex analytical challenge due to the following factors:

- The wide range of materials used for the construction of primary and secondary containers
- The diversity of physicochemical properties of the extracted and leached impurities
- Varying concentration levels in samples (ranging from pg/mL to µg/mL)
- Detection of these compounds in a wide range of different matrices.

To overcome these challenges, multiple and often complementary analytical techniques such as LC/MS, GC/MS, and ICP/MS as well as data processing and statistical tools are required. Recent publications have demonstrated the effectiveness of GC/MS [2] methodologies. Also, Norwood et al. [3], have reviewed numerous LC and LC/MS methods for the analysis of E&L.

Quadrupole time-of-flight (Q-TOF) mass spectrometers are suitable for this purpose due to their high resolution and accurate mass measurement capabilities.

An UHPLC Q-TOF system combined with statistical analysis software were used to detect and identify extractable and leachable (E&L) impurities from ophthalmic drug products. Statistical data analysis was performed to determine the compounds present in the samples compared to controls. The database search tool within statistical software helped to identify E&Ls using a customized accurate mass database. For the identification of unknown E&Ls, MS/MS data together with an structure prediction software, was used. In this study, 50 compounds were detected in each of the E&L samples.

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O-CPA-2

DETERMINATION OF METHOTREXATE AND ITS MAIN METABOLITES BY LC-UHR-QTOF IN HUMAN SERUM OF LEUKEMIA PATIENTS WITH HIGH-DOSE ADMINISTRATION

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High-dose Methotrexate (HD-MTX) treatment involves close monitoring of drug level in order to confirm its proper elimination. One of the possible side effects of this therapy is renal failure, causing accumulation of the drug and therefore a significant toxic effect. Glucarpidase (carboxypeptidase-G2 or CPDG2) is a recombinant enzyme used to reduce methotrexate serum levels in patients who develop acute renal failure during high-dose MTX treatment. The enzyme reduces MTX concentration by 95-99% within 15-30 minutes after dose. Glucarpidase cleaves methotrexate (MTX) into glutamate and 2, 4-diamino-N10-methylpteroic acid (DAMPA), a minor and non-active metabolite. Cross-reactivity of DAMPA in immunological assays of MTX has been previously reported, which causes an enormous overestimation in serum MTX analysis, however immunoassay is a widely technique for MTX analysis, being main methodology for its determination in most clinical laboratories.

This work describes the accurate determination of MTX and its main metabolites in serum samples by liquid chromatography coupled with Ultra High Resolution Q-Time of Flight Mass Spectrometry (LC-UHR-QTOF). Main objective was to overcome the interference of principal metabolites of MTX, and quantitate the actual concentration of the drug in a real case of an Acute Limphoblastic Leukemia patient under HD-MTX treatment. Sample preparation consisted in a protein precipitation with methanol and ultracentrifugation. MTX concentration in serum had to be monitored continuously until a level below 4.5 ng mL^{-1} was reached due to high drug toxicity. Due to the high sensitivity of the methodology the reached Limit of Quantification of MTX was below 0.2 ng mL^{-1} , without any interference caused by DAMPA or other minor metabolites, which were also monitored in order to stablish the metabolism profile in serum after Glucarpidase administration.

O-SP-1

DESIGNING NEW MICROEXTRACTION DEVICES FOR A BETTER USER-FRIENDLY ANALYTICAL APPROACH

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Bar adsorptive microextraction (BAμE) was introduced in 2010 and since then become a very attractive enrichment technology in particular for trace analysis of polar organic compounds [1]. This static microextraction approach operates under the floating sampling technology, which is a novel enrichment concept, and has proven to be easy and simple to manipulate, cost-effective, robust, as well as environmentally-friendly, being a potential alternative over other sorption-based techniques. Furthermore, this analytical approach enables to tuning the most convenient sorbent phase according to the target analytes involved, and requires a reduced sample volume and negligible amounts of organic solvent for the back-extraction step, in compliance with the green analytical chemistry principles [2]. Among several applications already performed, BAμE has been successfully assayed in the determination of many classes of priority compounds in matrices from areas with high impact in society at large such as environment, pharmaceutics, forensic and food [3].

Nevertheless, when static microextraction techniques, such as BAμE, are applied from semi-volatile to non-volatile compounds, the back-extraction stage used to be performed through liquid desorption (LD), which it is not the most straightforward approach in the practical point of view. In general, the LD needs up to six steps making this procedure the limitative stage, neither a user-friendly analytical approach nor ideal to interface with the instrumental systems. To overcome all these limitations, novel microextraction devices must be design, in particular as cost-effective approaches suitable for routine analysis.

The present contribution discusses all the advantages of the new generation BAμE devices that uses a more convenient design for an outstanding microextraction performance, as well as, for a better user-friendly analytical approach.

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O-SP-2

SYNTHESIS AND CHARACTERIZATION OF MAGNETIC COMPOSITES BASED ON MOFs INTENDED FOR MAGNETIC DISPERSIVE MICROEXTRACTION APPLICATIONS

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MOFs are porous hybrid materials composed by metal ions and organic linkers, presenting the highest surface areas known. The availability of various building blocks of metal ions and organic ligands makes possible (at least in theory) to prepare an infinite number of new MOFs with diverse structure, topology and porosity. These unique characteristics make them promising agents as extraction materials. More recently, they have been pointed out as potential sorbents in analytical extraction approaches, being used in several sample preparation approaches, particularly in micro dispersive solid-phase extraction (μ-DSPE).

In μ-DSPE the solid sorbent (<500 mg) is directly put in contact with the aqueous sample containing the target analytes, and dispersed with the aid of stirring, ultrasounds or vortex. It is possible to separate the extracted analytes linked to the sorbent from the remaining aqueous phase with the aid of magnet if the solid sorbent is associated with magnetic microparticles (MμPs), without the need of any further centrifugation or filtration step. Afterwards, a simple elution step of analytes form the sorbent is undertaken.

Magnetic particles (MPs) are characterized by their superparamagnetic properties. They are commonly composed by iron oxides, mainly magnetite (α-Fe_3O_4). MPs can either be bare (neat) Fe_3O_4, or can be coated and thus denoted as “core@coating” (i.e.: Fe_3O_4@SiO_2).

Fe_3O_4@MOF composites are very interesting materials because the sorbent material (the MOF) is attached to a particle that can be easily removed from the sample container with the aid of an external magnet. Due to the exceptional extracting properties of the MOF materials, a small quantity of these particles (Fe_3O_4@MOF) is needed. However, the controlled crystallization of the MOF on the surface of the MP represents a challenge.

The further use of the Fe_3O_4@MOF in microextraction methods for monitoring contaminants in environmental waters is the intended application.

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O-SP-3

MIXTURE OF ANIONIC AND CATIONIC EXCHANGE SORBENTS TO SIMULTANEOUSLY EXTRACT ACIDIC ANB BASIC PHARMACEUTICALS FROM ENVIRONMENTAL WATERS

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Solid-phase extraction (SPE) is the most commonly used sample treatment technique for liquid samples in analytical chemistry. One of the main advantages of SPE is the availability of different sorbents, which can enhance capacity (sensitivity) or effectiveness in the removal of interferences (selectivity). Among them, polymeric mixed-mode sorbents were developed to combine reversed-phase interactions and ionic interactions in a single material, with the objective of increasing selectivity in SPE procedures of different analytical methods [1]. There are several studies in which these mixed-mode sorbents, both prepared in-house and commercially available [2,3], have been successfully applied to extract different type of analytes selectively from complex samples, but so far, the success of these sorbents is limited to either basic or acidic compounds depending on whether cationic or anionic sorbents were used.

The aim of the present study is to broaden the application of these sorbents to both groups of compounds by combining for the first time the four different type of ion-exchange mixed mode polymeric sorbents, that is the strong-anion exchange (SAX), strong-cation exchange (SCX), weak-anion exchange (WAX) and weak-cation exchange (WCX), which turn out to be four single SPE cartridges: 1) SAX/SCX; 2) SAX/WCX; 3) SCX/WAX; 4) WAX/WCX; all of them with balanced positive and negative charges. The four cartridges were evaluated for the simultaneous extraction of a group of basic and acidic pharmaceuticals and the best combinations of sorbents were applied to develop improved and efficient methods based on SPE and liquid chromatography-high resolution mass spectrometry (LC-HRMS).

The experimental conditions were optimized in environmental samples in order to reduce the matrix effect present in LC-HRMS. A method using the best combination of sorbents was validated and applied to the determination of the pharmaceuticals in different environmental samples, such as river and influent and effluent wastewater samples.

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O-SP-4

SCREENING OF SYNTHETIC CANNABINOIDS IN ORAL FLUIDS BY BAR ADSORPTIVE MICROEXTRACTION

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The last decade has seen an increase of new psychoactive substances (NPS) that were been widely spread through "smart shops" and over the Internet. NPS are psychoactive substances not internationally controlled but may pose a similar risk to traditional drugs. In 2015, 98 new substances were detected for the first time in Europe, bringing the total number of NPS monitored to 568. Synthetic cannabinoids are one of most diffused NPS, since they are legal alternatives of *cannabis*. Since 2008, 160 new synthetic cannabinoids were detected in a wide range of different products - being 24 reported in the last year. Some of these compounds possess a 4 to 5 times improved binding affinity to the CB1 and CB2 receptors, when compared to tetrahydrocannabinol. Many toxicity symptoms were associated with the consumption of these drugs: anxiety, paranoia, tachycardia, irritability, hallucination, numbness, seizures, high blood pressure, drowsiness, slurred speech and in some cases even death [1].

For this reason, there is the need for innovative and alternative analytical approaches that allow an effective monitoring of these compounds in biological matrices, in particular using noninvasive samples such as oral fluids. In this contribution we present the development, optimization, validation and application of a novel methodology based on bar adsorptive microextraction (BAμE) [2], followed by microliquid desorption, in combination with high performance liquid chromatography with diode array detection for monitoring eight synthetic cannabinoids (AM-694, SGT-25, MAM-2201, 5F-UR-144, JWH-018, JWH-122, UR-144 and AKB-48) in oral fluids. This new analytical approach presents excellent extraction yields (70 - 100 %) with limits of detection in between 2.0 and 6.0 μg L^{-1} that proved to be an effective methodology for screening cannabinoids in oral fluids.

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OJ-FA-1

NOVEL GC-MS STRATEGIES FOR THE ACCURATE AND SENSITIVE SPECIATION OF SO_2 IN WINE

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Sulfur dioxide has been widely used in winemaking because of its antioxidant, antioxidasic and antiseptic properties. SO_2 may appear in wine under different forms due to its acid-base properties and to the more or less reversible adducts that it can form with acetaldehyde, sugars, polyphenols and other carbonyls. Speciation of this molecule is essential because its bioactive and antioxidant activities are extremely dependent on the specific chemical species. Total levels of SO_2 are important because of safety and legal reasons. Bound sulfur dioxide represents a complex pool of diverse molecules from which free SO_2 can be released. Such release, inevitably will have consequences on wine sensory properties, since the cleavage of SO_2 adducts will release anthocyanins, and sensory relevant aldehydes [1]. Bisulfite (HSO_3^-) is important due to its antioxidant and antioxidasic properties and molecular SO_2 (SO_2 plus H_2SO_3) is the most bioactive form and the main responsible for microbial stability. The reference method of aspiration/titration for determining free SO_2 fails when levels drop below 7-8 mg/L. Moreover, this method is based on an unspecific determination in which acid volatile compounds can produce interferences which can be important at low levels. Additionally, there are doubts about whether the free SO_2 determined by the reference method is all equally active, because it has been shown that wines with similar levels of SO_2 have different level of protection [2].
Three different methods based on GC-MS have been developed for the speciation of SO_2. Total forms are determined by HS-GC-MS of the acidified sample after incubation at 100ºC. Free and weakly-bound SO_2 is similarly determined but incubation is carried out at 40ºC. Similar results to the official method are achieved but limits of detection are much better (1 mg/L of free SO_2) and the method is free from interferences. Finally, molecular SO_2 is quantified also by HS-GC-MS analysis of an acidified fraction obtained by purging the wine with nitrogen and trapping SO_2 in an aqueous alkaline solution (pH 11.5). Results have demonstrated that between 10 and 80% of the free SO_2 measured by the reference method is in fact forming complexes with polyphenols which are cleaved during the analysis.

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OJ-FA-2

EXTERNAL CONTROL FOR SPME IN SOLID FOOD SAMPLES: ANALYSIS OF VOLATILE COMPOUNDS IN RAW BEEF

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Solid phase microextraction (SPME) is the most used technique for direct analysis of volatiles in solid samples due to its easy automation and implementation, but especially to its high sensitivity. For complex matrices, such as meat, comparisons among samples are usually found using just raw areas or area percentages. In the first case, there is no control over changes related to the fiber adsorption-desorption or the detector sensitivity. In the second case, the problem arises when all the compounds vary in the same way and, therefore, no differences between samples are observed. The difficulty in quantification lies on the heterogeneity of solid samples, associated with unspecific variations in sample-gas and gas-fiber distribution coefficients. Furthermore, fiber has to be changed among experiments that last for a long period of time. Little variations in fiber´s coating have a direct impact on the number of molecules adsorbed on it. Therefore, SPME is extremely sensitive to matrix variations and variations between fibers. Problems might be solved with an internal standard (IS) with similar distribution coefficients. Moreover, there are other considerations to be taken into account such as finding an appropriate IS with similar volatility and no coelution with any other compound with the same mass to charge ratio, and the development of the procedure for the addition of the IS to the sample.

This work presents a new strategy to control irreproducibility and to quantify 25 volatile compounds in raw beef by HS-SPME. In the proposed method, 4 g of raw beef knuckles (*rectus femoris*) were transferred to a 20 mL headspace vial and a PDMS/DVB fiber was exposed to the headspace of the sample for 40 min at 37 ˚C. Volatiles were analyzed in a GC-MS using a DB-WAXETR column. In the final developed strategy, dipropylene glycol control solution was analyzed by HS-SPME-GC-MS every 16 meat samples. This control solution contained one representative compound of each studied family in beef (alcohols, furans, saturated ketones, unsaturated ketones, saturated aldehydes, alkenals and acids) and two IS for monitoring control solution stability. Using the most selective mass for each control compound, response factors were calculated for each family. These response factors were subsequently applied to each compound that belonged to the same family. This strategy was able to control the quantification procedure even if the fiber, the column or the control solution changed, with DSR (%) below 12% in the control solution.

OJ-FA-3

COMPREHENSIVE ANALYSIS OF GOAT MILK OLIGOSACCHARIDES

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Goat milk is known to contain oligosaccharides (OS) structurally similar to those present in human milk and in higher concentrations than milks from other mammals. Different beneficial properties, such as prebiotic and anti-inflammatory effects or modulation of the immune system have been attributed to these carbohydrates [1].

It is know that goat milk oligosaccharides (GMO) are complex structures with different glycosidic linkages, degrees of polymerization and monomeric composition. Since bioactive properties are directly related to the chemical structure, there is a high interest in the study of these OS. However, little information about their detailed structures, concentrations and evolution during different lactation stages is available.

Hydrophilic interaction liquid chromatography (HILIC) is a powerful technique for the analysis of OS, providing an appropriate resolution and good peak shapes. Also, in recent years, the use of nano-liquid chip-based technologies mainly coupled to mass spectrometry (MS) or tandem MS (MS/MS) techniques have demonstrated to be extremely helpful for OS identification and it has been applied to milk characterization due to its high sensitivity and ability for compositional verification [1].

In this work, a methodology for the comprehensive characterization of GMO was developed. Goat colostrum samples were initially selected for methodoptimization since they are expected to have higher OS amounts than mature goat milk [2]. Defatted and deproteinized milk samples, previously treated by size exclusion chromatography (SEC) to remove lactose, were analyzed by nanoflow liquid chromatography-quadrupole-time of flight mass spectrometry (Nano-LC-Chip–Q-TOF MS). Up to 78 oligosaccharides were identified. As a second step, a hydrophilic interaction liquid chromatography coupled to mass spectrometry (HILIC-MS) methodology was developed for the separation and quantitation of the main OS, both acidic and neutral carbohydrates. The developed methodology was used for a detailed study of the evolution of GMO at different stages of lactation and different trends were observed depending on the type OS (acidic or neutral). To the best of our knowledge, this is the first time that a comprehensive characterization of GMO has been carried out.

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OJ-NP-1
USE OF HYBRID QUADRUPOLE-ORBITRAP HIGH-RESOLUTION MASS SPECTROMETRY FOR IDENTIFICATION OF FOUR NOVEL DESTRUXINS PRODUCED BY *METARHIZUM BRUNNEUM*

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Destruxins are secreted metabolites produced mainly by entomopathogenic *Metarhizium spp.* such as *M. anisopliae* and *M. brunneum*. These secondary metabolites are cyclic hexadepsipeptides composed of a α-hydroxy acid and five amino acid residues and they can be classified into seven subgroups named A, B, C, D, E, E-diol (Ed) and F depending on the hydroxy acid group. Since the first isolation of destruxins A and B from *M. anisopliae*, forty different destruxins have been identified in several fungal strains and they exhibit a wide spectrum of biological and insecticidal activities by virtue of their structure being considered as biological agents in pest control.

Until now, most of techniques to determine destruxins are based on liquid chromatography (LC) coupled to ultraviolet detection or mass spectrometry (MS). Specifically, UHPLC–MS/MS has been applied in fungal culture [1] and in different parts of a potato plant (root, stem, leaves and tuber) inoculated with *M. brunneum* (EAMa 01/58-Su strain) [2]. However, it could only achieve to detect only fifteen destruxins (A, B, C, D, E, Ed, Ed_1, A_2, B_2, D_2, E_2, Cl, DesmA, DesmB and DH-A), basing on previous information of fragmentations and relative retention times. Moreover, LC-MS/MS methodology cannot elucidate structure and differentiate between metabolites with isobaric molecular ions and/or competing fragment ions as in the case of destruxins.

In the present work, hybrid Quadrupole-Orbitrap mass spectrometer was applied for screening and identification of known members of these secondary metabolites, but also for structural elucidation of novel destruxins. Initially, the fragmentation pathway of destruxin A was established combining high resolution mass spectrometry (HRMS) and multiple stage MS data in order to establish a strategy for the identification of destruxins, for which reference standards were not available. Four novel destruxins, namely C_1, Ed_2 (a possible degradation product of destruxin E_2) and G and G_1 (members of a new subgroup, containing a 2-hydroxy-4-ethylpentane-1,5-dioic acid as hydroxy acid group), were structurally elucidated and identified in *M. brunneum* using HRMS/MS data and the established fragmentation pathway. Moreover, nineteen known destruxins including A, B, C, D, Ed, F, A_1, B_1, Ed_1, A_2, B_2, D_2, A_3, DesmA, DesmB, DesmC, $DesmB_2$ and two chloro-derivatives (Cl and E_2 chlorohydrin) could be unequivocally identified in this fungus strain. This study has also allowed to establish relative retention time and characteristic fragment ions that could be used for further method using low resolution mass spectrometry, in order to quantify these compounds.

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OJ-CPA-1

SOIL AND PLANT UPTAKE OF PHARMACEUTICALS: ANALYTICAL DETERMINATION

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Wastewater effluents are known sources of pharmaceuticals and personal care products (PPCPs) into the environment. The use of reclaimed water for crop irrigation is an extended practice in countries suffering from water shortages. Despite the associated benefits, this activity may result in soil and plant uptake of different organic chemicals present in the waters used for irrigation [1]. Through the transpiration stream, these compounds could be translocated from soil to plant tissues above the ground [2]. In the last years, several groups of research have investigated uptake of PPCPs by plants [3]. However, the use of different experimental designs (e.g., growth conditions, investigated compounds, or plant biology) makes difficult to compare them and reach conclusions. Moreover, the reliable quantitative analysis of this type of compounds in such complex matrices also represents a challenge on this topic of research.

In this study, we developed a reliable multi-residue analytical method to quantify different classes of pharmaceuticals (12 prescription drugs, 2 illicit drugs and 3 transformation products) in lettuce tissues and soil. In order to do that, different extraction techniques: pressurized liquid extraction (PLE), ultrasonic liquid extraction (ULE) and “quick, easy, cheap, effective, rugged, and safe” (QuEChERS), were evaluated. In all cases, analyte determination was performed by means of liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). This methodology will be applied to evaluate lettuce and soil uptake of the target pharmaceuticals after crop irrigation with reclaimed water.

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OJ-CPA-2
COUPLING MICELLAR ELECTROKINETIC CHROMATOGRAPHY WITH MASS SPECTROMETRY USING A VOLATILE SURFACTANT FOR THE THERAPEUTIC MONITORING OF BENZIMIDAZOLES IN ANIMAL URINE

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Therapeutic drugs monitoring in veterinary medicine is a useful tool to assess when an animal has attained therapeutic concentration of a particular drug depending on the administered dose [1]. This can be the case of benzimidazoles (BZs), which are anthelmintic agents widely used in the prevention and treatment of parasitic infections in livestock [2] but excessive concentrations of BZs in animal biological fluids can lead to congenic malformations, teratogenicity & pulmonary edemas [3].

In this work a novel method based on micellar electrokinetic chromatography-tandem mass spectrometry (MEKC-MS/MS) has been proposed and validated for the identification and simultaneous quantification of thirteen BZs in animal urine samples (sheep, cow and goat). Separation was performed in a bare fused-silica capillary (1 m total length, 50 µm i.d). The electrophoretic separation was achieved using a voltage of 25 kV and a temperature of 25 ˚C. The running buffer was an aqueous solution of 50 mM perfluorooctanic acid adjusted to pH 9.0 with ammonium hydroxide. Direct coupling of MEKC to MS is possible using because the perfluorooctanic acid used in the separation buffer is a volatile surfactant. The sample was hydrodynamically injected for 75 s at 50 mbar and the sample solvent was water, allowing an on-line preconcentration based on sweeping of the analytes. The coaxial sheath-liquid sprayer used for CE-MS coupling consisted of ethanol/water/formic acid (50:49.5:0.5,v/v/v) and was delivered at a flow rate of 1.7 mL min^{-1} by syringe pump. The ESI voltage was set to -4500 V (positive mode). Other electrospray parameters at optimum conditions were: nebulizer pressure, 6 psi; dry gas flow rate, 8 L min^{-1}; and dry gas temperature, 250 ˚C. An ion trap analyzer operating in the multiple reaction monitoring mode (MRM) was used for detection.

Under optimum conditions, sensitivity enhancement factors ranged from 50 to 181 for the studied compounds. The applicability of the proposed method was demonstrated by the determination of BZs in animal urine samples employing as sample treatment just a 1:10 dilution with water. Good linearity was obtained (R^2> 0.993) for all BZs. Recoveries for fortified samples were higher than 82.3 %, with RSDs lower than 7.6 %. The limits of detection were below 69.3 µg L^{-1}.

The main advantages of the proposed method are the simplicity of operation, the rapidity to achieve a very high sample throughput with low cost and reduced waste. This method can help veterinarians to customize the administered dose of BZs for each individual case.

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OJ-CPA-3

IN-VITRO METABOLISM EVALUATION OF THE TRYPTAMINE 5-MeO-MiPT USING HUMAN LIVER CELLS

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The use of new psychoactive substances (NPS) has dramatically increased in the last years. They have been reported in an important number of seized materials, making necessary the development of new methodologies for the determination of the consumption of these types of substances. Metabolism studies must be performed to obtain biomarkers in potential consumers. *In-vitro* metabolism studies using cell cultures, especially human liver hepatocytes, in combination with high resolution mass spectrometry has proved to be a useful methodology for the study and evaluation of metabolism behaviour of NPS. The use of human hepatocytes instead of liver microsomes allows the promotion of Phase I and Phase II metabolites, while using microsomes only Phase I metabolites could be obtained.

In this study, metabolites of the novel psychodelic tryptamine 5-MeO-MiPT were obtained after *in-vitro* cell culture and elucidated by liquid chromatography coupled to quadrupole-time of flight mass spectrometry (UHPLC-QTOF MS). Two human hepatoma cell lines (Hep3B and HepG2) that are commonly used to study the hepatic metabolism of xenobiotics were employed. For the metabolism experiments, cells cultured in t-25 flasks were exposed to 5-MeO-MiPT at 10 µmol/L at 37ºC (in 5 mL of culture medium) and samples were collected at 0, 1, 6, 12 and 24 hours of incubation. In addition, control hepatic culture with the compound vehicle was prepared under the same conditions used for the metabolic study and sampled at the same time intervals than the metabolic experience cell culture. In order to study the stability of 5-MeO-MiPT in the culture medium, 5 mL of this solution with 10 µmol/L of the compound was also prepared and stored at the same conditions of cell cultures, sampling at 0 and 24 h.

After protein precipitation with acetonitrile, organic solvent evaporation and reconstitution with mobile phase, extracts were injected into the UHPLC-QTOF MS system in both positive and negative ionisation modes. The resulting metabolites were detected and tentatively identified making use of the accurate-mass information provided by QTOF MS for both (de)protonated molecule and fragment ions, after comparing control and positive samples. Additionally, the common fragment pathway and mass defect filter strategies were also studied.

OJ-OT-1

EARLY METABOLIC CHANGES IN HEPATIC HEPARG CELLS TO ROSEMARY DITERPENES BY METABOLOMICS

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A great body of evidence has successfully linked natural occurring dietary phenolics to cell proliferation inhibition, and thereby these compounds are regularly referred to as anticancer. However, the ability of phenolics to exert clinical anticancer activities has been questioned due to the fact that experimental studies on cultured cell lines or animals cannot be easily extrapolated to cancer prevention or therapy in humans. One of the reasons is that these studies have often been conducted at concentrations far beyond those that can be achieved in humans for disease-prevention or therapy. In addition, high doses of phenolics consumption may even be harmful for our health. At high concentrations, phenolic compounds or their oxidation products may interact with proteins, carbohydrates, and minerals, which will exert toxicity. They also interfere with signaling pathways regulating relevant biological processes in cells. The inhibitory effect of rosemary diterpenes carnosic acid (CA) and carnosol (CS) on proliferation of colon cancer cells has been recently investigated at the transcriptomic, proteomic and metabolomic level in our laboratory [1-3]. These compounds have shown to prevent proliferation of different colon cancer cells at the medium-range micromolar concentrations (IG50 <40 µM), but they also exert cytotoxic effects on tumor cells at higher concentrations (LC50 >60 µM). The HepaRG cell line has been recently established as a model able to differentiate and display features of liver progenitor cells in vitro and useful for investigation of toxic responses in vitro [4]. In this work, CA, CS and rosmanol (RS) caused mild toxic effects (<20% cell death) at concentrations that are highly toxic in colon cancer cells. We applied a metabolomic approach, based on GC-TOF MS and UHPLC-TOF MS to investigate the early metabolic responses of differentiated HepaRG cells exposed to low toxicity exposures of CA, CS and RS. Statistically significant up and down regulated metabolites obtained using both analytical techniques were combined for further data interpretation of the potential molecular mechanisms of toxicity of rosemary diterpenes in HepaRG cells.

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OJ-OT-2

METABOLOMICS INVESTIGATION OF DRUG DEPENDENCE EMPLOYING LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY

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Recurrent drug intake produces drug dependence which has high impact in society as it affects millions of people around the world and causes about a quarter of a million deaths per year. Cocaine is the most commonly illicit psychostimulant drug used in Europe, and its deleterious effects affecting multiple metabolic pathways are well known. More than 95 % cocaine addicts combine cocaine with ethanol intake, what produces an increased sense of euphoria compared to the use of these two drugs separately. The combined effect of these two addictive drugs is still poorly understood which, in turn, limits our understanding of the physiological mechanisms of addiction. Metabolomics is a postgenomic discipline enabling a global, unbiased overview of the physiological/biochemical effects of the drug intake. In this work, we apply metabolomics for an untargeted survey of the effects of combined cocaine and alcohol exposure to laboratory rodents. The technique employed was Liquid Chromatography coupled to high resolution Mass Spectrometry due to its robustness, reproducibility, and sensitivity.

Using a combination of the non-supervised (PCA) and supervised (PLS-DA) multivariate analysis we explored and unraveled the metabolic differences among our experimental groups: cocaine alone, ethanol alone, cocaine plus ethanol, and the saline group (control). A subset of specific metabolites having high variable importance on projection values were selected and identified through their retention time and MS/MS spectra. The metabolic pathways which were affected by the combined drug exposure are discussed with special emphasis on amino acids metabolism.

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OJ-OA-1

DETECTION, EVALUATION AND CHARACTERIZATION OF NEW STEROID SULFATE METABOLITES

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The anabolic androgenic steroids (AAS) are a class of performance enhancing substances prohibited in sports by the World Anti-doping Agency (WADA). AASs are extensively modified by phase-I and phase-II metabolism and excreted in urine mainly as glucuronide and sulfates. Due to their long-lasting beneficial effects, utmost retrospectivity needs to be achieved by targeting the most long-term metabolites of each of the AASs. Sulfate metabolites have been described as long-term metabolites for some of them. Liquid chromatography-tandem mass spectrometry (LC-MS/MS) allows for the direct detection of AAS sulfates.

The aim of this study was to evaluate sulfate conjugated metabolites of different AAS. Several analytical strategies; neutral loss scan (NL), precursor ion scan (PI) and selected reaction monitoring (SRM) methods were developed to detect potential sulfate metabolites. These methods were based on characteristic ionization and fragmentation behavior of sulfates (e. g. NL of 80 Da, PI of m/z 97) and also on specific losses of the studied substances (e.g. NL of 36 Da or 15 Da). These approaches were applied to urine samples collected before and after administration of 4-chloro-metandienone and stanozolol.

Several new sulfate metabolites were directly detected in post-administration urines. SRM methods were optimized to monitor all identified metabolites and they were applied to excretion study samples obtained after the oral administration of 4-chloro-metandienone (n=2) and, samples after oral and intramuscular administration of stanozolol (n=6). The detectability of these new metabolites was compared with that obtained for the commonly monitored metabolites, currently detected by GC-MS or LC-MS/MS. The detected metabolites were characterized by mass spectrometry data, acquired by LC-MS/MS and/or GC-MS/MS, or by chemical synthesis.

Some of these metabolites can be alternative markers to improve the detection of AAS misuse compared to previously described metabolites. Therefore, incorporation of some of the detected metabolites into initial testing procedures for AAS is advisable to all anti-doping laboratories.

OJ-ENV-1

DETERMINATION OF PRIORITY AND OTHER HAZARDOUS SUBSTANCES IN RECYCLED RUBBER SPORT SURFACES BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY. STUDY OF THE ENVIRONMENTAL RISKS

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In last years the transformation of used tires in recycled materials such as playgrounds or different indoor and outdoor sport fields is growing due to their resistance but several studies has demonstrated the presence of heavy metals, and hazardous substances in these recycled materials [1,2] and some metabolites of these chemicals were found in human fluids [3].

This work is focused in the study of a particular sport surface, the football fields of artificial turf whose base consists in recycled rubber granules. The aim of this work is the determination of a broad range of multiclass organic compounds in the recycled rubber granules. The presence of hazardous substances in the air and in the runoff water put in contact with the surface was also studied, since these pollutants can be dragged through the runoff water and incorporated to soils and other environmental systems, posing a major environmental problem. In other way, the environmental concern that involves the incineration of the rubber granulate employing in these sport surfaces was also studied.

Twenty football pitches were analyzed by UAE and SPME. For the analysis of the air and the runoff water SPME was applied, followed by GC-MS and GC-MS/MS and not only target compounds were detected. Screening studies (GC-MS and HPLC-QTOF-MS) demonstrated the presence of several harmful compounds in the own surface and also in the air and in the runoff water, making the incorporation of these substances more accessible to the environment.

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OJ-ENV-2

UHPLC-API-MS/MS vs GC-MS FOR THE DETERMINATION OF SEMIVOLATILE FLUORINATED ORGANIC COMPOUNDS

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Fluorotelomer olefins (FTOs), fluorotelomer alcohols (FTOHs), perfluorinated sulfonamides (FOSAs) and perfluorinated sulfonamide ethanol (FOSEs) are semivolatile fluorinated organic compounds partially or totally saturated by fluorine atoms. The study about FTOHs, FOSAs and FOSEs has been increased in the last years as a consequence of their distribution and mobility in the environment and their capability to be degraded into the persistent organic pollutant PFOA and PFOS [1]. However, there are few works reported about FTOs although it has been suggested their degradation to perfluorinated carboxylic acids (PFCAs) [2].

The non-ionic fluorinated compounds can be analyzed by GC-MS but some of them show retention and sensitivity problems due to the high volatility and ionization efficiency. In this work, we evaluate different strategies to improve both the chromatographic and ionization behavior of these compounds for their simultaneous determination by both GC-MS and UHPLC-MS.

The chromatographic separation of fluorinated compounds has been studied using different GC capillary columns. The low retention of some of them made necessary the careful selection of the sample solvent to avoid the peak overlapping. For instance, methanol, dichloromethane or methyl *tert*-buthyl ether have been tested and methanol provided the best performance for all the compounds. The ionization behavior has also been studied using classical ionization techniques (EI, PCI and NICI) and the best performance was obtained when using EI as ionization source. Nevertheless, difficulties observed that may hinder the detectability by GC-MS are discussed in this work.

As alternative to the GC-MS determination, LC-MS was evaluated using APCI and APPI as ionization source for the analysis of the whole families of compounds. The effect of mobile phase composition (solvent and additives) on the response has been studied and the results indicated that APPI source showed the best sensitivity for FTOHs, FOSAs and FOSEs employing acetonitrile as organic solvent and a toluene post-column addition as dopant. Nevertheless, APCI showed the best sensitivity for FTOs, employing acetonitrile as organic modifier. Considering these results, chromatographic separation was optimized to provide a sensitive and selective LC-MS method as alternative to the GC-MS ones.

Both UHPLC-MS/MS and GC-MS methods were validated and evaluated their applicability to the determination of semivolatile fluorinated organic compounds in water and consumer products.

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OJ-ENV-3

ULTRA-HIGH RESOLUTION MASS SPECTROMETRY (FT-ICR-MS): THE EFFECT OF A WILDFIRE IN SOIL ORGANIC MATTER

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Vegetation fires are a global phenomenon occurring in tropical, temperate, Mediterranean and boreal regions. Up to 90% of all forest fires in the EU occur in Mediterranean countries [1]. Wildfires generally affect soil organic matter (SOM) that is the most reactive fraction, resulting in changes to several properties and functions [2]. One of the most recent techniques applied to SOM research is Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). This, together with graphic interpretation tools such as van Krevelen diagrams [3] may be also used to assess alterations to SOM caused by fire.

The site of study was a sandy soil under Cork oak (*Quercus suber*) vegetation in Doñana National Park (SW-Spain). Alkaline extracts of soil sieve fractions (coarse, 1-2 mm "CF" and fine, <0.05 mm "FF") collected in a burned (B) area and an adjacent unburned (UB) control site with the same physiographic conditions were studied. The instrument used was a Bruker Daltonics 12 Tesla Apex Qe FT-ICR-MS equipped with an Apollo II ESI ion source, operating in negative ion mode [4]. Unique molecular formulas were assigned to peaks using a MatLab script and the compounds detected grouped into 7 main chemical families [3].

Unburnt soil: compounds with high intensity in the lignin/tannin and carbohydrate-like regions were found for UB CF and in the lipid and protein-like regions for the UB FF. This suggests different degrees of SOM evolution with that in CF less altered with higher contribution of fresh material than that in FF; the latter believed to be subjected to higher microbial activity/humification processes.

Burnt soil: high relative intensity in the carbohydrate-like and lignin-like regions and new molecular formulas in the aromatic and condensed aromatics regions are found for the B CF, suggesting fresh organic matter inputs as well as contributions from a more recalcitrant carbon pool. In the B FF, two SOM sources of alteration were identified; i) biogenic (microbial) with high intensity of lipid/protein-like compounds, similar to UB FF and ii) pyrogenic compounds in the condensed aromatic region together. This indicate both, condensation processes yielding black carbon like materials and additions from new chemical biogenic compounds i.e. from shifts in the microbial activity after fire or from fire mediated distillation processes.

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OJ-ENV-4

CONTRIBUTION OF FIREWORKS, FIRECRAKERS AND OPEN BURNING IN SPANISH POPULAR CELEBRATIONS TO CHLORINATED POPs IN AIR

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In order to investigate the potential release of some persistent organic pollutants (POPs) into the atmosphere from fireworks, as well as from firecrackers and open burning taking place at Spanish popular celebrations, an ambitious sampling campaign of ambient air was devised in Valencia and Barcelona at the celebration of *Fallas* and *Saint John's night*, respectively.

Here we present some preliminary results obtained from the sampling of ambient air at *Fallas*, one of the most unique popular celebrations in Spain involving the use of massive amounts of fireworks and firecrackers and the combustion of hundreds of constructions of paper, waxes, wood and polystyrene foam disseminated throughout the city of Valencia (south east Spain).

High volume air samplers were used for the sampling of gas and aerosol phases by means of polyurethane foams (PUFs) and quartz microfiber filters, respectively. Samples (PUFs and filters) were spiked with ^{13}C-labeled standards and Soxhlet extracted. Subsequent cleanup was carried out by means of the "Supelco Dioxin Prep System-Florisil Version". PCBs, PBDEs and PCDD/Fs were quantified by GC-HRMS on a Trace GC Ultra gas chromatograph (Thermo Fisher Scientific, Milan, Italy) coupled to a high resolution mass spectrometer (DFS, Thermo Fisher Scientific, Bremen, Germany). Positive electron ionization (EI+) was used operating in selected ion monitoring mode (SIM) mode at 10,000 resolving power. PeCB and HCB were analyzed by GC-LRMS using a 7890 N gas chromatograph coupled with a 5975C quadrupole mass spectrometer (Agilent, Palo Alto, CA, USA) operating in SIM and working with EI. Quantification was carried out in all cases by the isotopic dilution technique.

As preliminary results and in comparison with background control points, several patterns could be observed: 1) PCB levels in both gas and aerosol phases were relatively unaffected by the events of open burning and fireworks, 2) HCB and PCDD/F concentrations with values (in pg/m^3) of 29.4 and 47.0 in gas phase and of 0.271 and 874 in aerosol phase, respectively, peaked at the 4th day of *Fallas* celebration in clear correlation with the occurrence of open burning throughout the city but not of that of fireworks or firecrackers.

Further characterization of these contaminant levels with different air parameters will be carried out, including aerosol organic carbon content and air masses analysis. Moreover, comparisons with sampling performed at *Saint John's night* at Barcelona need to be established in order to find solid and common patterns.

OJ-ENV-5

FORECASTING SOIL ORGANIC CARBON SEQUESTRATION BASED ON THE INCREASED COMPLEXITY OF PYROLYTIC METHOXYPHENOLS

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Despite considerable progress during the past decades in the knowledge of the factors presumptively involved in soil carbon sequestration, additional research is required to establish the variability of these factors in space and time. Such knowledge is crucial to progress in the development of the scientific bases of Earth's biogeochemical cycle and global change. For this reason, we intend to find out useful proxies from soil organic matter characteristics or other soil properties which could play a role in soil carbon sequestration. For this study, we collected topsoil samples from up to 35 Spanish soils with different carbon content, geological substrate, vegetation and use.

The study of soil organic matter composition was carried out by pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) of whole soil samples. This technique displays a large potential to identify and asses relative proportions of the different organic compounds present in the soil. The technique does not require any pretreatment or previous sample extraction.

Methoxyphenols are typical pyrolysis products from soil organic matter, with an origin from plant biomacromolecules mainly lignin. Major methoxyphenols in soils correspond to 4-*H*-, methyl-, ethyl-, vinyl- and propenyl derivatives of guayacol and syringol. We apply several multivariate data treatments aiming to explain the total amount of soil organic matter in the different soils (dependent variable) as a function of the composition of its pyrolysis products. In particular and in order to express the complexity of the molecular composition of the different pyrolysis compounds, we applied the Shannon-Wiener biodiversity index, classically used to characterize species diversity in a community. In this research, the 'species' selected are the different methoxyphenols. Partial least squares regression exclusively using the total abundances of methoxyphenols yielded highly significant ($P< 0.01$) forecasting models which explain the concentration of organic C sequestered in the different soils. This leads to the suggestion that significant correlation exists between effective soil C storage and the more or less advanced stages of transformation of the organic matter. In fact, when the Shannon biodiversity index was calculated for the 12 major methoxyphenols, a significant correlation was found with the total organic C stored in the soils. This finding suggests that C sequestration behave as a soil emergent property which is reflected by the sources, complexity and interactions of the soil organic matter constituents at a molecular level, which would result into the accumulation of recalcitrant C-forms with increasingly chaotic structure, i.e., not readily recognized by soil enzymes.

OJ-NDI-1

DETECTING ACIDIC PPCPs IN SEWAGE WATERS BY LIQUID CHROMATOGRAPHY HIGH RESOLUTION MASS SPECTROMETRY

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Pharmaceuticals, illicit drugs and personal care products (PPCPs) are emerging pollutants widely distributed in water and their presence is highly studied [1-3]. The aim of this study is to apply triple quadrupole (QqQ) and quadrupole/Time-of-Flight (QqToF) Mass Spectrometers [4] to determine these compounds in sewage water using a common extraction procedure. The chromatography was performed with a 1260 Infinity HPLC in tandem with a 6410 triple quadrupole MS/MS both from Agilent Technologies (Santa Clara, CA, USA) using for compound separation a Kinetex C18 analytical column of 2.1 x 50 mm and 3.5 µm particle diameter from Phenomenex (Torrance, CA, USA). On the other hand, a HPLC of the same model than before, using an Agilent Poroshell EC-C18 maintained at temperature of 30º, coupled to a hybrid QqTOF ABSciex Triple TOFTM 5600 from Sciex (Concord, Ontario, Canada). The optimal mobile phase for both mass spectrometer was a gradient of 2.5mM Ammonium fluoride in water (mobile phase A) and 2.5mM Ammonium fluoride in methanol (mobile phase B), with a flow rate of 0.2ml min-1. The gradient starts with 30% of mobile phase B, increases until 95% at min 12 and is maintained for 13 min. The analytes were extracted from 250 mL of water by solid-phase extraction using Strata-X cartridges, eluted with methanol, evaporated, and dissolved in 250 µL of methanol: water (30:70). This procedure provides acceptable recoveries (70% - 115%) and relative standard deviation (RSDs < 20 %) at the limits of quantification (5-120 ng/L), which are in the low ppb range ensuring sensitivity enough. Some of the studied compounds were detect at low amounts in the analysed water, which establish the real environmental occurrence of these potential contaminants. The matrices objective of this study were the Turia River basin (water, sediments and soils), Valencian Waste Water Treatment Plants (Pinedo I and II and Quart-Benager) and drinking waters (tap and bottled water). Turia River was selected because it is a typical Mediterranean River heavily affected by drought. This River is a 280-km Mediterranean River with a flow rate 10.43 m3/s, which is born in the province of Teruel and flows near the Valencia city.

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OJ-NDI-2

OVERCOMING MATRIX EFFECTS IN SMALL MOLECULE ANALYSIS BY LC-MS USING NANOFLOW LC AND HIGH DILUTION FACTORS

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The determination of small molecules such as pesticides, environmental contaminants, veterinary and human drugs, and other species such as drugs of abuse or sport drugs has been usually carried out by ultra-high performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS) using electrospray ionization and reversed-phase chromatographic separations with analytical size columns. In this sense, the main drawback of electrospray ionization for quantitative studies is the occurrence of matrix effects (ME). Several strategies have been proposed to overcome, minimize or compensate ME during quantitative analytical LC–MS measurements. The main approaches are the improvement of the chromatographic separation, the application of specific dedicated clean-up protocols, the use of isotope dilution mass spectrometry or matrix dilution. However, this last option is restricted by the sensitivity of the instrument. So, high matrix dilutions cannot be applied to improve the ME. An interesting approach to improve the sensitivity in LC-MS with electrospray detection is downscaling the LC-MS method by using lower mobile phase flow rates. This strategy provides not only an enhancement in sensitivity, but also it can be used for increasing the ruggedness of methods by means of, for instance, the dilution of the sample extracts, thus minimizing ME. Nevertheless, the use of nano LC-MS has been restricted so far to selected bioanalytical applications, bearing in mind the difficulties associated to adapt such specialized approaches to routine applications.

This communication reports the evaluation of ME in challenging matrices such as food extracts, human urine or wastewater at different dilution factors using nanoflow liquid chromatography-high resolution mass spectrometry (LC-MS). For this purpose, a suite of representative low-molecular weight compounds such as pesticides, drugs of abuse or environmental contaminants were selected. The approach is based on the use of reversed-phase C18 nano columns furnished with a nanoemitter tip. The nanoflow LC system was combined with full-scan high resolution mass spectrometry using a Q-Exactive Orbitrap instrument operated at a resolution of 70000. From the results obtained, the sensitivity achieved with this configuration enables the implementation of high dilution factors (eg. 1:20, 1:50 or beyond). With this dilution factors, signal suppression was negligible in most cases (< 10 % in most cases, especially with 1:50 dilution), so that matrix-matched standards may eventually be skipped, thus simplifying laboratory workflows.

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OJ-SP-1

TRENDS IN ANALYSIS OF OXIDATIVE HAIR DYES

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Hair dying is an increasingly practice among women and men covering a wide range of ages. Attending to the different categories of products for colouring hair, oxidative hair dyes are by far the preferred by consumers for their long-lasting properties, and therefore they dominate the global market in the sector. Oxidative or permanent hair dyes are uncoloured or faintly coloured compounds but when they are mixed in the presence of an oxidant, frequently a solution of hydrogen peroxide, they produce coloured complexes. These precursors, referred as intermediates and couplers, are essentially aromatic ring derivatives such as diamines, aminophenols, phenols or naphthols. Most of these ingredients are categorized as potent contact allergens and despite various attempts by the cosmetic industry to introduce chemicals with lower allergenic potential, a recent study [1] evidences a still high number of contact allergies caused by hair dyes, including some banned substances by EU Regulation [2]. Hence, the development of selective and sensitive analytical methods for the control of hair dyes is necessary in order to safeguard the product quality and consumer safety.
In this work, the influence of the sample treatment in the analysis of oxidative hair dyes is studied. Procedures based on vortex extraction (VE), ultrasound-assisted extraction (UAE) and matrix solid-phase dispersion (MSPD) will be fully validated and applied to commercial samples. Optimized conditions involve low sample amount and reagent consumption as well as simpler equipment and handling requirements compared to previous methodologies. Since the high reactivity of hair dyes, their stability is tested and the addition of antioxidants is performed. Gas chromatography coupled to tandem mass spectrometry is applied to the analysis of the extracts obtained, previously derivatized by acetylation. The use of tandem mass spectrometry provides great analytical selectivity and sensitivity. It is important to highlight that this is the first time that a GC-MS/MS method is developed to the analysis of hydroxylated dyes such as dihydroxybenzenes, their derivatives, and naphthols.

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OJ-SP-2

SIMPLE AND EFFECTIVE MULTIRESIDUE METHOD FOR 5-NITROIMIDAZOLE ANALYSIS IN FISH ROE SAMPLES BY UHPLC-MS/MS

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5-nitroimidazoles (5-NDZs) are a wide-spectrum antibiotic class used for treating infections due to anaerobic protozoan and bacteria, however, their use in veterinary medicine has been restricted within European countries according to Regulation (EU) No 37/2010 [1]. Alerts about their presence in animal products destined to human consumption are still notified by the Rapid System of Food and Feed (RASFF) portal, so analytical methods are required for 5-NDZ determination in order to ensure food safety. A novel multiresidue method has been proposed for the determination of twelve 5-NDZs in fish roe samples by UHPLC-MS/MS. A salting-out assisted liquid-liquid procedure has been proposed for the extraction of the analytes. Moreover, the variables that affected the separation such as the mobile phase composition and flow rate as well as the parameters involved in the ionization and fragmentation for MS detection were studied in detail. Finally, the separation was accomplished in a C18 Zorbax Eclipse Plus (50 mm × 2.1 mm, 1.8 µm) column using a mobile phase consisted of 0.025% (v/v) formic acid aqueous solution (eluent A) and MeOH (eluent B). Mobile phase was supplied at 0.5 mL/min and column temperature was set to 25°C. Samples were injected in mobile phase (5/95 (v/v) MeOH:0.025% (v/v) formic acid aqueous solution), and an injection volume of 17.5 µL was considered. The proposed method was characterized in terms of linearity (R^2 ≥0.9996), extraction efficiency (≥71.4%), repeatability (≤9.8%), reproducibility (≤13.9%) and trueness (≥72.3%). Decision limit (CCα) and detection capability (CCβ) values between 0.3-1.5 and 0.5-2.5 µg/kg, respectively, were obtained for all 5-NDZ compounds. The reached results accomplish with the requirements of Regulation (2002/657/EC) and the recommendations of European Union Reference Laboratories for the determination of these substances.

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P-FA-1

VACUUM-HEADSPACE SOLID-PHASE MICROEXTRACTION FOR THE DETERMINATION OF FREE FATTY ACIDS AND PHENOLS IN MILK AND MILK DERIVATIVES

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Solid phase microextraction (SPME) is a successful technique that provides simple, fast, and sensitive extractions of analytes from complex samples [1]. In their headspace mode (HS-SPME), the analytes use the gas phase as an intermediate phase between the sample and the SPME fiber. Thus, volatile and semi-volatile compounds, characterized by high Henry's law constants (K_H), are preferentially extracted and preconcentrated with this methodology.

Different strategies have been applied to enhance HS-SPME extraction kinetics of less volatile compounds. They include: (i) the application of stirring and high temperatures, (ii) the assurance of a large sample/headspace interface, or (iii) the use of the cold fiber HS-SPME approach [2]. The use of reduced-pressure conditions during the HS-SPME extraction has also been introduced as an alternative to these modifications. This new methodology, termed as vacuum-HS-SPME, is particularly convenient for the extraction during the non-equilibrium stage of HS-SPME, and for semi-volatile organic compounds (or those with low K_H values) [3].

The main aim of this work is the development of a vacuum-HS-SPME application for the determination of a group of volatile and semi-volatile compounds, specifically free fatty acids and phenols, which are responsible (among other compounds) of the aroma of milk and milk derivatives. With this purpose, a new homemade device has been developed to carry out the HS-SPME extraction under reduced pressure. The approach also combines the use of stirring and heating. Different SPME fibers have been tested for the monitoring of these compounds, including commercial SPME fibers but also polymeric ionic liquids (PIL)-based fibers. The vacuum-HS-SPME approach was combined with gas chromatography and flame ionization detection (GC-FID) for monitoring the selected compounds in milks and milk derivatives.

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P-FA-2

POLYMER-BASED MATERIALS MODIFIED WITH MAGNETITE NANOPARTICLES FOR ENRICHMENT OF PHOSPHOLIPIDS

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Sample preparation methods generally involve a solvent- or solid-phase (SPE)-based extraction technique. However, these conventional extraction procedures have some disadvantages, e.g. long extraction time, column blocking, limited selectivity, poor reusability, etc. In this sense, the development of new SPE sorbents with enhanced properties is highly desirable.

In the last years, magnetic nanoparticles (MNPs) have attracted much research interest due to many potential technological applications such as drug delivery, adsorption processes and environmental remediation [1]. Also, MNPs can be used as a novel and excellent adsorbents due to their unique advantages over traditional microsized adsorbents [2]. Thus, a novel procedure for SPE, based on the use of magnetic or magnetically modified adsorbents called magnetic solid-phase extraction (MSPE) has been recently developed. A distinct advantage of this technology is that magnetic materials can be readily isolated from sample solutions by the application of an external magnetic field.

The phospholipids of milk and dairy products are concentrated either in the milk fat globule membrane; however, they constitute only a small proportion of the total lipids in milk. Besides, their extraction, separation and detection are critical points in the analytical approach. Thus, the development of selective and efficient extraction methodologies is mandatory.

In this study, a methacrylate-based sorbent modified with magnetite nanoparticles (Fe_3O_4) was developed as platform for capture of phospholipids in human milk samples. Scanning electron microscopy and Fourier transform infrared spectroscopy were applied to the characterization of Fe_3O_4 and these bare MNPs onto the polymeric support. The effect of several experimental parameters of MSPE on the extraction performance of the target compounds was investigated. The recommended method was applied to the extraction and determination of these compounds in human milk fat samples.

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P-FA-3

DEVELOPMENT OF MOLECULARLY IMPRINTED POLYMERS FOR SOLID-PHASE EXTRACTION OF PHOSPHOLIPIDS IN HUMAN MILK SAMPLES

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Milk is the most important food for the newborn due to its unique nutrient composition, immune components, and metabolic enzymes, which all contribute to meet the critical requirements to support a normal growth and development of term infants. Human milk contains 3–5% fat, including a small proportion of polar lipids (approximately 1% of total lipids), namely phosphoglycerides and sphingolipids. These compounds are important constituents of milk fat globule membrane and play an important functional, structural and metabolic role. However, the analysis of these components usually requires several separation/pre-concentration stages from the bulk sample are therefore efficient methodologies based on solid-phase extraction (SPE) have been proposed [1]. However, advances in the selectivity of these solid sorbents should be highly desirable.

Molecularly imprinted polymers (MIPs) have been shown to offer excellent selectivity for those compounds used as template molecules during the MIP synthesis. After removal of the template molecules, recognition cavities complementary to the template molecule in shape, size and chemical functionality are formed in the highly cross-linked polymer matrix. Since the available volume of human milk samples is limited to a few milliliters, small SPE formats are more suitable for performing the pre-concentration process. The aim of the current work is the development of a MIP sorbent for phospholipids and its application for human milk samples. The resulting polymer was used as SPE sorbent for direct extraction of phospholipids. Several experimental variables that can influence on the extraction efficiency were identified and studied in detail. Under optimized conditions, a rapid, selective and cost-effective method for the extraction and determination of phospholipids was established by coupling the MIP technique with hydrophilic interaction liquid chromatography.

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P-FA-4

GC-MS AND HPAEC-PAD CHARACTERIZATION OF PECTIC OLIGOSACCHARIDES (POS) DERIVED FROM HYDROLYSIS OF CITRUS AND APPLE PECTINS

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Pectins are one of the most structurally complex families of polysaccharides in nature [1] and are isolated on an industrial scale mainly from apple and citrus peels [2]. Besides, these pectins are widely used as functional food ingredient. Pectic oligosaccharides (POS) are obtained by depolymerisation of pectins by chemical, enzymatic and combined methods. POS include various types of oligomers, i. e. oligogalacturonides (OGalA), galacto-oligosaccharides (GalOS), arabino-oligosaccharides (AraOS), rhamnogalacturono-oligosaccharides (RhaGalAOS), xylo-oligogalacturonides (XylOGalA) and arabinogalacto-oligosaccharides (AraGalOS) [3]. The structural characterization of POS is very difficult however different chromatographic methods have been developed for their characterization such as HPAEC-PAD [4] and GC [5]. Therefore, the aim of this work was to characterize by GC-MS and HPAEC-PAD of POS obtained by enzymatic hydrolysis of citrus and apple pectins using two commercial enzyme preparations. POS were obtained by enzymatic hydrolysis of 1% (w/v) of commercial citrus and apple pectin using 16 U/mL of Glucanex 200 G and 4 U/mL of Viscozyme L preparations. Depolymerisation reactions were followed by HPLC-SEC-RID and GC-FID. Then, optimal conditions of hydrolysis were selected and POS formed were characterized by HPAEC-PAD and GC-MS. According to the results obtained by HPAEC-PAD maximum POS formation was achieved at 30 min of hydrolysis ranging from to 448.9 to 929.3 mg/g pectin. Digalacturonic and trigalacturonic acid were identified among other minor compounds. Molecular weight of POS varied from 0.2 to 9.6 kDa (HPLC-SEC-RID). GC-MS allowed determining *m/z* ions 217, 332 and 540 corresponding to galacturonic acid fragments in all samples. In addition, *m/z* ions 423, 321 and 277 derived from β-cleavage fragmentation of uronic acids were reported in small abundance. Citrus and apple pectins behave similarly, however the two enzymatic preparations studied produced different chromatographic profiles of POS.

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P-FA-5

COMPARATIVE STUDY OF ANIONIC COMPOUNDS FOUND IN NATURAL AND PROCESSED JUICES ANALYZED BY CE-MS

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Nowadays juices are an important source of nutrients, since they provide energy in the form of sugars from fruit (fructose mainly), vitamins (vitamin C and carotenes mostly) and mineral salts (magnesium, phosphorus). In addition, processed juices, which used to be consumed in Spanish households, retain in nearly similar proportions almost all fresh fruit nutrients due to their processing improvements. Fruit juices have different concentrations of organic acids that can be used as a "fingerprint" to establish their authenticity. For example, tartaric acid is normally used as an indicator of grapefruit juice addition to other more expensive juices, like orange juice. As well, isocitric acid has been used as a marker to assess the authenticity and quality of citrus fruits juices [1]. Therefore, quality controls are needed to verify label information.

The main objective of the present work consisted in the identification of anionic compounds present in 6 natural and 6 processed orange juices, as well as the determination of potential adulterants. Time of flight-mass spectrometry coupled to capillary electrophoresis (CE-MS) was used to identify and quantify compounds. Separations have been performed in a COSMOS capillary (100 cm x 50 µm id), using reverse polarity with ammonium acetate 50 mmol/L as background electrolyte at pH 8.5 [2].

88 compounds in natural and 91 in processed juices were characterized. 38 of them showed significant differences between groups of juices: only 3 were present in processed juices, and 14 appeared in lower and 21 in higher concentrations in processed juices respect to naturals. In addition, the presence of tartaric acid was detected in processed juices, pointing out a grapefruit juice possible adulteration.

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P-FA-6

CHARACTERIZATION OF TMS DERIVATIVES OF GLYCOSYL-INOSITOLS BY GC-MS

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Glycosyl-inositols are constituted by one or several (up to four) galactosyl residues and an inositol or a methyl-inositol. These compounds are especially abundant in legumes but they can be found in seeds of other plants such as buckwheat or pine nuts. Several bioactive properties, mainly associated with insulin resistance, have been attributed to them [1].

Up to now, HPLC and GC [1,2] have been used for glycosyl-inositol analysis, but no comprehensive method is available for the characterization of these compounds, probably due to the lack of enough adequate standards. GC-MS can provide valuable qualitative and quantitative information for the characterization of these compounds along with other soluble carbohydrates, after derivatisation and avoiding tedious fractionation processes. Linear retention indices (I^T) are only available for a very few glycosyl-inositols [1] and a systematic study of their mass spectra (MS) is also lacking. Therefore, the aim of this work was to correlate the chemical structure of different glycosyl-inositols with their I^T values and MS data in an attempt to help in further identification of unknown compounds.

Several glycosyl-inositols with different structures (derived from *chiro-, myo-*, and methyl-inositols, and also mono-, di- and triglycosyl- compounds) from plant extracts (buckwheat, chickpea and grasspea) were considered as standards. Different saccharides were used for comparative purposes. These compounds, previously derivatised, were analysed by GC-MS using a methylsilicone capillary column.

Regarding GC retention, galactosyl-cyclitols derived from *chiro*-inositol eluted before those derived from *myo*-inositol. Moreover, galactosyl-cyclitols (degree of polymerization (DP) 2) eluted within sucrose and raffinose, digalactosyl-cyclitols (DP3) within raffinose and stachyose and trigalactosyl-cyclitols (DP4) were eluted within stachyose and verbascose. MS data revealed a lower abundance of ion at *m/z* 361 for glycosyl-cyclitols compared to saccharides. Ratios of *m/z* ions 133/129, 260/265 and 375/361 were proposed for the first time in this work to distinguish glycosyl-inositols from glycosyl-methyl-inositols, as they allowed the unequivocal characterization of them. Results have afforded the characterization of different non-previously identified glycosyl-cyclitols appearing in chickpeas, adzuki beans and leaves of *Coriaria myrifolia* and *Coriaria ruscifolia*.

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P-FA-7

DETERMINATION OF CURCUMIN AND RELATED COMPOUNDS BY HPLC-UV. APPLICATION TO THE CHARACTERIZATION AND AUTHENTICATION IN TURMERIC PRODUCTS

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Turmeric (*Curcuma longa*) is a plant related to ginger family that has been used for centuries as a remedy of traditional Asian pharmacy. Nowadays, turmeric is used worldwide for different purposes such as in medicine due to its great antioxidant and anti-inflammatory properties, in cuisine as an interesting condiment and colorant, in chemistry as a labelling dye, etc. In particular, the rhizome is the part with highest commercial interest and it is typically sold as dried portions or as a powder. Among other ingredients, curcumin has been recognized as one of the relevant molecules of turmeric, providing both color and activity to the products. Recently, an increasing suspicion has arisen about fraudulent adulteration of turmeric products. As a result, analytical methods for authentication turmeric and quantification of curcumin in different kind of samples are necessary to protect consumers from possible frauds and medical concerns.

In this work, a chromatographic method for the determination of curcumin in turmeric samples has been developed. The method relies on the separation of the analyte and side curcuminoids by reversed phase HPLC with UV detection. The separation column was a Kinetex C18 (100 mm × 4.6 mm i.d., particle size 2.6 µm) furnished with a SecurityGuard C18 cartridge (both from Phenomenex, Torrance, CA). An elution gradient based on 0.1% (v/v) formic acid aqueous solution and MeOH as the components of the mobile phase was used. The flow rate was 1 mL min^{-1} and the injection volume 10 µL. Chromatograms were recorded at 280, 310 and 370 nm.

The method was applied to determine the content of curcumin and related compounds. Commercial samples of different origin were analyzed and compositional profiles and chromatographic fingerprints were used as the analytical data to be used in characterization. Further studies will be carried out to try to deal with classification and authentication issues using chemometric methods.

P-FA-8

CHARACTERIZATION AND CLASSIFICATION OF SPARKLING WINES BY LIQUID CHROMATOGRAPHY AND CHEMOMETRIC METHODS FOR DATA ANALYSIS

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Cava is a high quality sparkling wine with Protected Designation of Origin (PDO) produced by the *Champenoise* method based on second fermentation and aging in the bottle. In this project, the compositional profiles of polyphenols and the chromatographic fingerprints established by liquid chromatography have been exploited as the data to be treated by principal component analysis (PCA). The determination of polyphenols in wines is of great interest in the field of food analysis due to health and organoleptic implications. Besides, the relevance of polyphenols as descriptors of food features is gaining popularity to deal with characterization, classification and authentication issues. It has been described that compositional profiles of polyphenols in wines are dependent of factors such as geographic origin, grape varieties, winemaking practices, etc. [1]

In this work, a simple and reliable method based on HPLC separation in reversed phase mode with UV-Vis detection has been developed and applied to determine polyphenolic compounds in cava wines. The chromatographic separation has been performed by using a C_{18} column under a methanol elution gradient assessed by an experimental design approach. Analytical parameters have stablished under the optimal experimental conditions. Limits of detection are below 100 µg L-1 and repeatabilities are better than 1% for most of the analyzed polyphenols.

The proposed HPLC-UV method has been applied to characterize Cava wines produced from different grape blending and sugar contents. Compositional data have been further used to perform characterization studies based on chemometrics. PCA results have demonstrated that wines can be discriminated successfully according to grape varieties.

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P-FA-9

MONITORING THE VOLATILE PROFILE OF EXTRA VIRGIN OLIVE OILS FROM PICUAL AND HOJIBLANCA VARIETIES GROWN UNDER THREE CONDITIONS: CONVENTIONAL IRRIGATION, DRY FARMING AND ORGANIC PRODUCTION

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The increase in demand for virgin olive oil is not only due to its health properties but also to its organoleptic properties, which ultimately determine consumer preferences and choice. In native cultivars, it is essential to assess the impact of the ripening stage on the agronomic parameters, volatile profile and the quality of the resulting virgin olive oil for optimal exploitation of the grove [1]. Furthermore, irrigation positively influences the composition and organoleptic characteristics of olive oil [2]. However, previous studies have shown that olive variety and ripening stage have a greater effect than the method of cultivation [1].

In this context, the aim of this work was to monitor the volatile profile of extra virgin olive oils obtained from Picual and Hojiblanca olive varieties grown under conventional irrigation, dry farming and organic production, and harvested at four different ripening stages. In addition, it aimed to study the relationship among volatile compounds in the maturation process, the varietal influence and different cropping systems.

The volatile profile of each obtained olive oil was determined by gas chromatography-mass spectrometry (GC-MS) with a prior extraction step using a magnetic stir bar called Twister® (*GERSTEL GmbH & Co. KG*) in the headspace of the sample (Headspace Sorptive Extraction "HS-SE"). Principal Component Analysis (PCA) was performed to evaluate whether the volatile profile were great enough to distinguish the different kind of extra virgin olive oils analyzed in this study. Hence, samples were differentiated by their variety, growing conditions (ecological irrigation differed markedly from conventional treatments) and the stage of ripeness of the fruit (the longer this stage was, the more differences existed).

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P-FA-10

COMPARATIVE ASSESSMENT OF SOFTWARE FOR NON-TARGETED DATA ANALYSIS IN THE STUDY OF THE VOLATILE FINGERPRINT CHANGES DURING STORAGE OF A STRAWBERRY BEVERAGE

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Food aroma is a mixture with a huge number of volatile compounds. The most studies until today investigated volatile profile of food following a targeted approach, where a particular set of compounds are monitored. Usually, these targets are selected based on prior knowledge such as literature records [1]. Currently, there has been a growing interest in non-targeted data analysis. In a non-targeted approach all compounds are potentially of interest without any a priori hypothesis. This methodology has been recently applied to the study of changes on volatile composition in kiwifruit puree [1] or a mixed puree of tomato and carrot [2]. The data pre-processing of a non-targeted approach is generally composed by different important steps: deconvolution, library-based identification, and peak alignment of chromatograms [3]. There are available different software to perform deconvolution, alignment or both. For that, the aim of this work was the evaluation and comparison of the different programs to assess their suitability for non-targeted evaluation of the impact of storage on the volatile fractions of a strawberry beverage. For this purpose, a strawberry beverage obtained by gluconic fermentation was prepared [4]. Several aliquots of this were stored at different temperatures, in the fridge and at room temperature (25 °C), and samples were taken at different times. In this study, we analyzed the initial sample and samples with 60 days of storage. Volatile profiles were determined by dynamic headspace gas chromatography-mass spectrometry (DHS-GC-MS). The deconvolution of chromatograms was performed using AMDIS program. The optimization of AMDIS deconvolution setting for data was performed according to [5]. We have compared the following software SpectConnect, MetaboliteDetector, MassHunter, Gavin, among others. In some cases, we observed high variability between peak area values for some volatile compounds in the duplicated analyses of the same sample using certain software.

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P-FA-11

ANALYSIS OF DITHIANON BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY COUPLED TO TRIPLE CUADRUPOLE TANDEM MASS SPECTROMETRY

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The risk to the health of consumers associated with the use of pesticides is becoming a consumers' concern, since they can remain after application as residues in food. That is why strict quality control of pesticide residues in food is commonly used to ensure food safety. This study has been focused on the determination of dithianon, which is widely used in a variety of fruits and vegetables. Dithianon is a compound that acts as a contact fungicide with preventive action, with great adherence and persistence. This compound is effective against the black spots of apples and pears caused by a broad spectrum of fungi. Consequently, and due to its toxicity, the presence of their residues in food should be evaluated [1]. In the present study an analytical method has been developed and validated for determining dithianon in apples and pears by liquid chromatography coupled to tandem mass spectrometry, achieving a fast (running time = 7 min) and reliable method.

The samples of apples and pears were extracted applying a QuEChERS extraction procedure (Quick, Easy, Cheap, Effective, Rugged and Safe). For optimization of the extraction method three versions of QuEChERS method were compared (in apples and pears): original, American and European. The best results were obtained with the European QuEChERS method. In order to reduce the number of interference in the extract, and therefore to minimize the cleaning stages of the QqQ analyzer, a cleaning step was incorporated using different sorbents (primary secondary amine (PSA), C18, graphitized carbon black (GCB) and a mixture of the three applied sorbents). The most useful cleanup was obtained with 50 mg of PSA. According to SANTE guidelines [2] satisfactory validation parameters were obtained. The validation parameters estimated were: linearity, recovery (ranged between 85 to 87% in pears and 82 to 97% in apples), precision (repeatability and reproducibility) (obtained values ≤ 14% for both matrices), limit of detection (LOD) (0.5 µg kg^{-1} in apples and pears), limit of quantification (LOQ) and retention time window (RTW). The applicability of the method was proved during the analysis of real samples of apples and pears, detecting this compound in one of the real apple sample.

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P-FA-12

INFLUENCE OF OLIVE WASHING ON THE VOLATILE PROFILE OF AN ORGANIC EXTRA VIRGIN OLIVE OIL

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Extra virgin olive oil quality depends on many different factors such as olive variety, olive tree cultivation and the olive picking, storage and processing [1]. The olive washing is a preliminary step commonly used in olive oil production to remove foreign materials and leaves from olives. It is one of the important operations that could influence the mechanical safety of the olive and the organoleptic quality of olive oil [2].

For this reason, this study aims to evaluate the influence of the olive washing process on the volatile profile of an organic extra virgin olive oil. The first step was to randomly selecting 60 olives samples belonging to the Picual variety (the most important olive variety in Spain) and grown under organic production in an early season harvesting. The corresponding olive oils were obtained using these selected olives, half of them with a prior olive washing process and the rest without a washing olive operation.

The volatile profile of each obtained olive oil (with olive washing and without olive washing) was determined by gas chromatography-mass spectrometry (GC-MS) with a prior extraction step using a magnetic stir bar called Twister® (*GERSTEL GmbH & Co. KG*) in the headspace of the sample (Headspace Stir Bar Sorptive Extraction "HS-SBSE"). Different chemometric methodologies were applied to the whole chromatograms, such as Parallel Factor Analysis 2 (PARAFAC2) or Multivariate Curve Resolution (MCR) and Principal Component Analysis (PCA), to obtain further information of the chromatograms and to increase the knowledge of the possible influence of the process of washing olive in the olive oil's volatile profile.

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P-FA-13

A COMPARATIVE STUDY OF THE VOLATILE PROFILE OF WINE VINEGARS WITH PROTECTED DESIGNATION OF ORIGIN BY SORPTIVE EXTRACTION TECHNIQUES

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Some wine vinegars have been traditionally linked to a specific geographical area and the European Union has protected them with a legal framework called “Protected Designation of Origin” (PDO). In recent years, three PDO wine vinegars have been registered in the south of Spain: “Vinagre de Jerez” (“Sherry wine vinegar”), “Vinagre Condado de Huelva” and “Vinagre Montilla-Moriles”. Furthermore, within each PDO, there are different categories according to their aging time and type in wood barrels.

Aroma is considered one of the most important indicators of vinegar’s quality. The raw material, the production process and the ageing in wood barrels determine the unique quality and organoleptic properties of each wine vinegar. Despite the fact that some authors have previously studied the volatile profile of Sherry vinegars, scarce research has been done to assess the volatile composition of these three PDO vinegars[1]. Gas chromatography-mass spectrometry (GC-MS) is the most employed technique for analysing volatile compounds, but it is necessary an extraction step prior to GC-MS analysis. Classical extraction techniques used are time-consumer and expensive. For that reason, there is an increasing tendency in the development of new extraction methods with better detection and quantification’s limits, faster and no-consume solvents[2].

In this context, the volatile profile of different PDO wine vinegars (“Vinagre de Jerez”, “Vinagre Condado de Huelva” and “Vinagre Montilla-Moriles”) was analysed. Three advantageous extraction techniques in conjunction with GC-MS (Headspace Solid Phase Microextraction “HS-SPME”, Headspace Stir Bar Sorptive Extraction **“**HS-SBSE” and Dynamic Headspace Sorptive Extraction “DHS-SE”) were evaluated for this purpose. Further methodologies such as multi-sample Multivariate Curve Resolution (MCR) and Principal Component Analysis (PCA) were applied to the whole chromatogram to obtain the maximum information of the volatile profile and the extraction techniques.

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P-FA-14

A SENSITIVE, QUANTITATIVE ANALYSIS OF MINOR COMPONENTS IN DEODORIZATION DISTILLATES OF VEGETABLE OILS

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Deodorization oil distillates (DOD) are the most valuable by-product of the refining process of vegetable oils. The refining of oils enables the elimination of color, odor and flavor that make the crude oils unacceptable to consumers. In addition, chemical compounds that might be toxic or those that decrease the oil stability are removed in the refining process. Unfortunately, other components, including phytosterols, tocopherols and squalene, of well-known bioactivity, are removed in part along with the undesired compounds and are ultimately concentrated in the DOD [1].

The composition of DOD varies greatly depending on the starting oil, the type of refining process, chemical or physical, and the operation conditions applied. Typically, the average composition by weight of a deodorizer distillate is as follows: 30–35% free fatty acids, 20–40% glycerols, 2–10% tocopherols, 3–15% sterols, 2–5% hydrocarbons, 3–10% non-glyceride esters and 1–12% miscellaneous substances [2]. A proper control of raw materials is essential to ensure that the subsequent processing provides a product that meets the required specifications. Difficulties of analysis arise from such a heterogeneous mixture of compounds. The most applied analysis for the determination of the global composition of DOD is gas chromatography after sample silylation [3,4]. However, one-step analyses might be inaccurate due to possible chromatographic overlappings between different groups of compounds.

In this work we feature an analytical procedure that improves the composition analysis of DOD in terms of accuracy. The method is based upon a previous fractionation of the DOD sample by solid-phase extraction on a bonded aminopropyl silica phase. Three fractions were obtained. A nonpolar fraction contained Hydrocarbons, Alkyl Esters and Triacylglycerols. An intermediate polar fraction comprised partial glycerides, Mono-and Di-acylglycerols, tocopherols and sterols as the main groups. And a third final fraction formed by free fatty acids (FA) was isolated using acidic conditions. For a detailed analysis of specific compounds, the separated fractions were finally analyzed by GC. Squalane, α-5-cholestanol and pentadecanoic acid were used as internal standards, given the different response factors for the main groups of compounds in each fraction. The separation of the FA in the third fraction improved the quantification of sterols and tocopherols in the second fraction not only because of the absence of chromatographic overlappings, but also because of a significant concentration effect. Repeatability and recovery of the method were determined.

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P-FA-15

STUDY OF CLEAN PROCEDURES TO APPLY QUEChERS TO DETERMINE PESTICIDE RESIDUES IN COFFEE LEAVES

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In recent years pruning of tree branches has increased in coffee plantations, in an attempt to increase production of coffee beans. The leaves of these branches could be used for production of coffee leaf tea, instead of being removed from plantations and burned. There is already in the market coffee leaves from organic plantations, and up to our knowledge no works have been done describing the analysis of pesticide residues in this matrix.

A QuEChERs based method was used as first step extraction procedure of pesticide compounds from coffee leaves in order to determine and quantify the follow pesticides commonly used in coffee plantation: buprofezin, chlorfenviphos, coumaphos, fenitrotion, fluvalinate, parathion ethyl, parathion methyl, thiametoxam. Extraction was performed with acetronitrile and clean up with: A: 50 mg of PSA, 50 mg C18 and 50 mg CGC; B: 50 mg of PSA, 50 mg C18 and 50 mg ZEP. For selection of the best clean up DLLME was also tested. The experiments were also performed using 5 mL of ultrapure water with 1 mL of acetonitrile extract of QuEChERS (after d-SPE with 50 mg of PSA and 50 mg C18) and 100 μL of extraction solvent (trichloromethane and tetrachloromethane). Pesticides determination was achieved using ultra high performance liquid chromatography coupled to triple quadrupole tandem mass spectrometry (UHPLC- QqQ-MS/MS), operating in positive ionization mode. Total running time was 25 min. Data were processed using a MassHunter Workstation Software for qualitative and quantitative analysis.

We clearly could observed that methods A and B show the same profile for thiametoxam, and gave highest peak area for most of pesticide under study, DLLME clean up gave a very poor extraction and also recovery. In relation to thiametoxam recovery the same good profile was obtained for all methods, but for the rest of the pesticides the DLLME clean up again gave very poor recoveries. Therefore either method A or B could be selected as the clean up method. The clean up procedure apply to extract these selected pesticides from coffee leaves samples shows the applicability of QuEChERS and the sensitivity obtained using UHPLC- QqQ-MS/MS to determine pesticides in coffee leaves.

P-FA-16

DETERMINATION OF ESTROGENIC COMPOUNDS IN MILK AND YOGURT SAMPLES BY HOLLOW-FIBER LIQUID-PHASE MICROEXTRACTION-GAS CHROMATOGRAPHY-TRIPLE QUADRUPOLE MASS SPECTROMETRY

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Lately, substances exhibiting natural or synthetic estrogenic activity have become of concern, since they can be introduced in the environment but also in the human food chain. These compounds may mimic the activity of endogenous hormones or even interfere with them [1, 2].

In this work, an eco-friendly method based on hollow-fiber liquid-phase microextraction (HF-LPME) was developed for the extraction of selected estrogenic compounds (*i.e.* four natural sexual hormones -estrone, 17β-estradiol, 17α-estradiol and estriol-, two exoestrogens -17α-ethynylestradiol, 2-methoxyestradiol-, two synthetic stilbenes -dienestrol, hexestrol-, and five resorcylic acid lactones -zearalenone, α-zearalanol, β-zearalanol, α-zearalenol and β-zearalenol), from whole cow and semi-skimmed goat milk and whole natural yogurt.

After the optimization of the sample preparation procedure, spiked extracts were derivatized to their trimethylsilyl products using N,O-Bis(trimethylsilyl)trifluoroacetamide reagent and then analyzed by gas chromatography–tandem mass spectrometry (GC-MS/MS). Once optimum extraction conditions were established (protein precipitation with acetonitrile, extraction and them desorption following the HF-LPME procedure) the method was validated and the calibration range, precision and accuracy were studied. The RSD values for the intra- and inter-day precision of the peak areas were in the range 0.65-9.69 % and 1.00- 11.47%, respectively. The determination coefficients higher than 0.991 for method calibration curves while LODs and LOQs values were between 0.06-2.55 µg/L and 0.16-6.11 µg/L for whole cow milk, 0.04-1.70 µg/L and 0.11-4.86 µg/L for semi-skimmed goat milk and 0.07-3.73 µg/L and 0.23-9.81 µg/L for natural yogurt, respectively. Finally the accuracy and precision of the method was evaluated obtaining a value in the range 81-119% and RSD values lower than 20% in all cases.

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P-FA-17

PRESENCE OF PLASTICISERS AND PRESERVATIVES IN DAIRY PRODUCTS BY UHPLC-ESI-QqQ(MRM). INFLUENCE OF STORAGE AND PACKAGING

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Food safety is a main priority for food industries and for consumers' health protection authorities. Consequently an increasingly pressing demand to know and control the possible presence of toxic compounds in food exists. Among the exogenous and toxic chemical compounds that must be controlled in foodstuffs, plasticisers such as phthalates (phthalic acid esters, PAEs) and bisphenol A (BPA), and preservatives such as parabens, have received special attention in the last few years due to the clear evidence of their toxicity. All of them are considered Endocrine Disrupting Chemicals (EDCs) because of their ability to interfere and disrupt several aspects of the endocrine system physiology in laboratory animals, wildlife, and humans[1,2,3,4].

This work presents the results of the analysis of **four phthalates** (PAEs: dimethyl phthalate, diethyl phthalate, dibutyl phthalate and butyl benzyl phthalate), **seven parabens** (PBs: methyl paraben, ethyl paraben, *n*-propyl paraben, *iso*-propyl paraben, *n*-butyl paraben, *iso*-butyl paraben and benzyl paraben) and **bisphenol A** (BPA) in 49, 24 and 32 commercially available low-fat-content samples of yogurt (Y), cream (C) and cheese (Ch) respectively. Because of contamination problems, a simple and fast method for the simultaneous extraction and purification was applied. Briefly, a single step of extraction plus clean-up was carried out in in a glass column by matrix solid phase dispersion (MSPD) using Florisil® as a dispersant agent put on a layer of Florisil® (purification). The column was eluted with ethyl acetate and concentrated for the final determination by ultra-high performance liquid chromatography coupled to triple quadrupole tandem mass spectrometry (UHPLC-QqQ(MS/MS)).

Different types of containers (polystyrene (PS), polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), high-density polyethylene (HDPE), glass, metallic spray, carton packages and aluminium with vinyl chloride and vinyl acetate) and different commercial brands (**Y,** n=11; **C,** n=6; **Ch,** n=7) have been investigated. Those containers that were not identified by the manufacturer were characterised using infrared spectrophotometry in attenuated total reflectance (ATR-IR) mode.

In most cases, the highest concentration levels (expressed as median in pg/g fresh weight) were found for PAEs, followed by PBs and BPA, except for cheese samples, which had higher concentrations of PBs. Different concentrations of PAEs, PBs and BPA were found, depending on the type of sample analysed and the container used. For example, yogurt samples packaged in HDPE containers (baby food) presented the lowest PB concentrations. Relating to cream samples, the highest BPA concentrations were found for metallic spray containers, which agrees with the use of epoxy resins in this type of packaging. Regarding cheese samples, concentrations of BPA were considerably higher in samples packed in aluminium with an internal coating of vinyl chloride and vinyl acetate (cheese portions) than in the rest of packaging types.

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P-FA-18

ANALYSIS OF SEED OILS STEROLS AND FATTY ACID COMPOSITION BY METHYLATION AND COMBINATION OF CHROMATOGRAPHIC TECHNIQUES

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Food authenticity is claimed by more and more demanding consumers. Regarding edible fats and oils, fraudulent blends that include cheaper commodities resemble the genuine material at an extent that the fraud detection should be based on a thorough knowledge of changes in characteristic constituents of the oil concerned and the use of complex statistical methods. The fatty acid composition in combination with the composition of sterols is a main identity characteristic of fats and oils. Sterols or the so called phytosterols in vegetable oils form part of the unsaponifiable fraction and are minor, highly specific components. In standard analytical methods, the oil is saponified and the unsaponifiable fraction is obtained by solvent extraction. The phytosterols are normally isolated from the unsaponifiable matter by TLC. Then they are sylanized and analyzed by GC. The whole procedure is time consuming and therefore not recommendable for routine analysis.

In this work, we propose a simple, rapid method for accurate quantification of both the fatty acid composition and the composition of sterols in seed oils. The method consists in the transmethylation of the oil to transform the triacylglycerols into fatty acid methyl esters (FAME), fractionation of the treated oil by solid phase extraction (SPE), sylanization and GC analysis. Compared to the standard method, the analysis proposed is quite more rapid and requires much smaller volumes of solvent.

In the SPE step, two fractions of different polarity are obtained. The non-polar fraction comprises hydrocarbons and the FAME, whereas the polar fraction is formed by sterols as the main group of compounds. Analysis of both fractions by GC enables the determinations of the fatty acid composition and sterols, respectively. The internal standard method is used for quantification purposes. The recovery of the analytes and the repeatability of the quantitative results are examined in the present work.

P-FA-19

DETERMINATION OF AROMATIC POLYCYCLIC HYDROCARBONS METABOLITES IN MILK SAMPLES, USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-FAST SCANNING FLUORIMETRIC DETECTION

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Hydroxy-polycyclic aromatic hydrocarbon derivatives (OHPAHs) are metabolites of the polycyclic aromatic hydrocarbons (PAHs). The hydroxylated PAHs metabolites considered as biomarkers are: 1-hydroxy-, 2-hydroxy-, 3-hydroxy-, 4-hydroxy-, and 9-hydroxyphenantrene, 3-hydroxybenzo[a]pyrene, 2-hydroxyfluorene and 1-hydroxypyrene, and they are the ones chosen for this study. These metabolites have can be detected in biological fluids such as urine and plasma but also in milk [1, 2]. However, bibliographic references were not found about of analysis of these metabolites in human breast milk.

A deep research about the possible methods for extraction and purification of these hydroxyl-polycyclic aromatic hydrocarbons derivatives was carried out, with milk samples of different origins, both woman's breast milk and cow milk of different types: full-cream milk, semi-skimmed milk, skimmed milk and daily milk. All the compounds mentioned before are known as biomarkers of risk exposure of polycyclic aromatic hydrocarbons and hitherto they haven't been analyzed in a single chromatographic run in milk samples. This is why we decided to establish a chromatographic method, and a previous extraction procedure to analyze fortified milk samples with all these analytes.

Several milks were tested by spiking known quantities of OHPAHs and remaining in contact during 24 hours. Later, de-conjugate enzymatic reaction were applied to separate the analytes from milk matrix, and a cleaning step was carried out by liquid-liquid extraction with acetonitrile. Samples in acetonitrile were analyzed by HPLC-FSFD method. The final outcome proved that the analytes can be properly separated from woman's breast milk, with a good yield for all of the compounds. The limits of detection ranged between 0.07 ng mL^{-1} and 3.43 ng mL^{-1} for 2-hidroxy-+3-hydroxyphenantrene and 3-hydroxybenzo[a]pyrene, respectively. The rest of the tested milks also showed a good yield, ranging between 70 and 100% in most of the cases. Therefore, this new method can be applied as a valid method for extraction, separation and analysis of OHPAHs in milk samples of different origins.

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P-FA-20

PROFILING FOOD VOLATILES BY DIRECT COUPLING OF THERMAL DESORPTION AND MASS SPECTROMETRY. DIFFERENTIATION OF THYME CHEMOTYPES

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Sample characterization based on its volatile composition is a topic of high relevance in the food science and technology field for different purposes such as authentication of samples, quality control, etc. Gas chromatography coupled to mass spectrometry (GC-MS) has become the analytical technique of choice to carry out this sort of studies. However, the interest in analytical platforms which allow the analysis time (mainly associated with the chromatographic separation) to be reduced has promoted the development of non-separative approaches based on direct injection MS (DIMS) for the high throughput and cost-effective characterization of food samples. DIMS strategies have mostly addressed the discrimination of food samples for authentication tasks or the prediction of different food quality parameters from MS fingerprints. Nevertheless, the number of contributions aimed at quantitative analysis is much more limited.

The present work has been developed to establish the real possibilities and limitations of quantitative profiling of volatiles in food samples by DIMS in combination with multivariate regression methods: namely, multiple linear regression, stepwise multiple linear regression, ridge regression (RR), principal component regression and partial least squares regression. The most relevant factors affecting quantitation were first evaluated on simulated data. Then, as an example of application on real samples, experimental mass spectral fingerprints collected by direct thermal desorption coupled to mass spectrometry (DTD-MS) were evaluated for the quantitation of major volatiles in *Thymus zygis* subsp. *zygis* chemotypes.

In general, the performance of all regression methods with DTD-MS data was good, giving rise to very low root mean square error of prediction (RMSEP) values. Moreover, errors obtained for every specific compound and chemotype were very similar irrespective of the regression procedure considered (between 2 and 10% in most cases). RR was the only method tending to outperform over the rest. This could be explained by the high collinearity between mass spectra and the good performance of RR method for 'ill-conditioned' data. The results obtained, validated with the DTD-GC-MS method here used as reference, show the potential of DIMS approaches for the fast and precise quantitative profiling of volatiles in foods.

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P-FA-21

PHOTOCHEMICAL STUDIES OF UV IRRADIATION OF FOLATES. POS-COLUMN ON-LINE PHOTODERIVATION FOR THE DETERMINATION OF FOLIC ACID AND ITS METABOLITES.

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Folates are important for human nutrition and health, being important to know their content in food. In order to differentiate and quantify individual folate forms, a High Performance Liquid Chromatography (HPLC) method with fluorimetric detection is proposed. Fluorescence has not been frequently used with these purposes, because only some reduced forms of folates, such as tetrahydrofolic acid (THF) and 5-methyltetrahydrofolic acid (MTHF), exhibit native fluorescence. Folic acid (AF) itself is not fluorescent, but when folic acid solutions are UV-irradiated, an increase in the fluorescence intensity is observed, because their photoproducts are fluorescent. [1]

We have studied the fluorescence changes that occur when FA and its metabolites are irradiated by using an *off-line* UV lamp. The photo-processes were monitored by LC-FLD, with aliquots of the irradiated solutions. The influence of variables such as pH, irradiation time, presence of H_2O_2, and absence of O_2 has been studied. The main photoproducts for each of the analytes have been identified by LC-ESI/MS.

When FA is irradiated for a short time, the main fluorescent photoproduct formed is pterin-6-carboxylic acid, but when increase the irradiation time, pterin was detected as the main photoproduct. Moreover, others non fluorescent photoproducts have been identified corresponding with the loss of the glutamate moiety, of the pteridinic group moiety or both. The formation of photoproducts from THF and MTHF do not involve modification in their fluorescence spectral characteristics due to the scarce formation of pteridine derivatives. For THF, the loss of the glutamate is the principal way of decomposition, giving rise to the formation of fluorescence photoproducts with very similar chemical structures to the parent folate. For MTHF, it is remarkable the formation of the OH-derivative in 4a position, and the increment in the fluorescence quantum yield observed.

Moreover, an *on-line* post-column photoderivatization chromatographic method has been developed for the analysis of FA, THF and MTHF. Linearity ranges from 50 to 1000 $ng{\cdot}mL^{-1}$ for FA and from 100 to 1000 $ng{\cdot}mL^{-1}$ for THF/MTHF were established. Detection limits of 7.5 $ng{\cdot}mL^{-1}$, 15.3 $ng{\cdot}mL^{-1}$ and 22.9 $ng{\cdot}mL^{-1}$ for FA, THF and MTHF respectively, were calculated. The method has been satisfactorily applied to cereals, spinach and tomato samples.

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P-FA-22

EVALUATION OF ENDOCRINE DISRUPTING PLASTICISER MIGRATION IN HOUSEHOLD FOOD CONTAINERS

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Plastics are of general use and different plasticisers are employed in their fabrication. Of special concern is the use of those plasticisers acting as endocrine disrupting compounds (EDCs) in the fabrication of household food containers and the migration of certain EDCs to the food itself. EDCs are chemical substances that may interfere the endocrine system. While some of these plasticisers are already controlled by certain regulations, others are relatively new and unknown. Among those plasticisers that produce endocrine disorders, phthalates, bisphenols and their derivatives are the most widely used.

We designed experiments in order to study these possible migrations. Different factors were considered, *i.e.* type of food (using food simulants [1]), type of food container (disposable, bisphenol A (BPA)-free and glass containers), type of conservation (fridge or freezer, for different periods of time), as well as their use in the microwave (heating up, deep heating up, defrosting and reuse). A total of 96 food containers with 250 mL of food simulants were prepared and their contents were directly analysed by UHPLC-QqQ(MS/MS) [2] in the search of 6 phthalates: dimethyl (DMP), diethyl (DEP), dibutyl (DBP), butyl benzyl (BBP), diethylhexyl (DEHP) and di-*iso*-nonyl phthalate (DiNP), 3 bisphenols: BPA, bisphenol B (BPB) and bisphenol F (BPF) and 6 diglycidyl ether derivatives of BPA and BPF: (BAGDE, BFDGE, BADGE·H_20, BADGE·$2H_20$, BADGE·HCl and BADGE·HCl·H_20).

Results showed migrations of specific plasticisers from the household container to the food simulants. The migrations depended on the type of simulant, the type of food container, as well as, the type of conservation, time and use in the microwave. In general, all the concentrations found were low, below 4 ng/mL of simulant. The most remarkable findings are: i) among the six phthalates studied, DEP and DBP were the most frequently detected; ii) concentrations found in plastic food containers were similar to those found in glass food containers; and iii) BPA-free containers did not show the use of other alternative bisphenols (such as BPB and BPF).

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P-FA-23

AUTHENTIFICATION OF IBERIAN HAM USING VOLATILE COMPOUNDS BY HEADSPACE-GAS CHROMATOGRAPHY-ION MOBILITY SPECTROMETRY

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The Iberian pig constitutes a breed of great economic importance in Spain. Iberian pigs are raised under different rearing systems and their dry-cured products such as ham are classified in two different categories, *acorn* or *feed*, depending on their feeding. *Acorn* ham comes from pigs raised in free-range finishing with a diet of acorns and grass, while *feed* ham comes from pigs raised in confined farm and fed with concentrated feed. This causes great differences in quality and final prices implying that Iberian ham is susceptible to fraud.

Consequently, several analytical procedures have been proposed to ensure Iberian ham authenticity. They are essentially based on fatty acid determination using gas-chromatography flame-ionization detection, near-infrared signal, ultrasonic measurements, or liquid-chromatography coupled to high-resolution mass spectrometry (HRMS) [1]. Although, the study of volatile fraction by headspace-gas chromatography-MS [2] has also been used for ham classification. However, these techniques are expensive and time-consuming, and hence impractical for the routine control of meat samples. Thus, other vanguards techniques such as electronic nose [3] and ion mobility spectrometry (IMS) with UV source [4] have been used in the last years with this purpose.

This work continues to explore the potential of IMS for differentiation of *acorn* and *feed* ham as a first approach to Iberian ham authentication. In particular, a radioactive ionization source (^{3}H) and the coupling to a chromatography column (GC) for pre-separation before analysis have been proposed. Samples were introduced by headspace-gas.

A total of 25 samples (13 *acorn* and 12 *feed*), previously classified by a group of experts tasting panel, were analysed. Topographic plots for volatile compounds were acquired using two GC (non-polar and polar column) and data were processed by two chemometric methodologies. A first approach consisted on the establishment of individual markers that appeared along the spectra and the chemometric treatment was carried out using SIMCA-P software. The model (OPLS-DA) classified 100% and 98.2% of samples using non-polar and polar column, respectively. The second approach consisted on the processing of the complete spectral fingerprint. Spectrum regions containing the most of information were selected and after pre-processing step a multivariate analysis was performed using MATLAB and PLS toolbox software. In this case, 100% and 95.6% of samples using non-polar and polar column, respectively, were classified. These results provide promising perspectives for the use of IMS to differentiate ham samples according to their quality.

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P-FA-24

A COMPENDIUM OF FOOD AND BEVERAGE COMPARISONS WITH A NOVEL BENCHTOP GC-TOFMS SYSTEM

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GC-TOFMS is an analytical technique that is broadly applicable for food and beverage samples. Among other capabilities, it offers the non-targeted characterization of samples and the ability to target specific analytes of interest in order to compare and contrast various samples. The performance of a novel benchtop GC-TOFMS system is demonstrated here for a variety of food and beverage products. A collection of food and beverage samples (fresh and dried herbs, fresh and frozen produce, flavored candies, flavored beverages, hops, and wines) were prepared for analysis with HS-SPME (using a DVB/CAR/PDMS fiber). The samples were subsequently analyzed with GC-TOFMS and characterized for both targeted and non-targeted.. The various volatile and semi-volatile analytes that contribute to the aroma and flavor of the products were collected with HS-SPME and separated with GC. The samples were successfully compared and contrasted using a novel benchtop GC-TOFMS system. Deconvolution offered an additional level of information based on the mathematical separation of the full m/z range TOFMS data. This aspect of the analytical approach allowed for identifying and quantifying individual analytes even when chromatographically co-eluting with other analytes in the matrix. In some cases, these co-elutions were important sample distinguishing features that would be hidden without this capability. Several examples are demonstrated. A novel GC-TOFMS system with improved sensitivity and linear dynamic range is well suited for routine screening applications and non-targeted characterization of samples for discovery applications

P-FA-25

MONITORING CARBOHYDRATE PROFILES OF COCOA BEAN FERMENTATION

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Fermentation of cocoa beans from "Theobroma cacao" is a crucial step in the formation of precursors for the characteristic flavor and aroma of cocoa.

A better understanding of the biochemical reactions that take place during fermentation including carbohydrates, polyphenols, lipids and amino acids allow for an enhanced control of the first cocoa processing steps. In particular, monitoring the changes of carbohydrates during fermentation is of high interest because the reducing carbohydrates, together with amino acids are involved in the formation of flavor and aroma compounds via Maillard Reaction.

For the present study, six fermentation series were investigated which differ in their origin and procedure. Three spontaneous fermentation series from Ecuador, Brazil, and Ivory Coast were sampled every 24h for 5 and 6 days. In addition, a special local fermentation process from Ecuador was investigated, which is characteristic for drying samples prior to fermentation. Finally, two laboratory fermentation series were analyzed, derived from a forced fermentation (without yeast) and an artificial fermentation (constant temperature of 35° C and increase in pH over time).

The analysis of the carbohydrates by Hydrophilic Interaction Liquid Chromatography coupled to ESI-TOF-MS of the different fermentation trials under study showed that the concentration of sucrose, raffinose and stachyose decreases during the fermentation of cocoa beans. This observation could be a consequence of the reduction of pH during fermentation of cocoa beans (6.64 to 4.7 in samples from Ivory Coast). This reduction is the result of different factors such as migration of the different organic acids produced by microbial activities from outside to inside of the cocoa seeds [1].

Principal component analysis of the data allows to (i) separate different fermentation procedures, and (ii) follow the time course of the fermentation. It is perceptible how the fermentation produces changes in the profile of the carbohydrates. The samples from forced fermentation and artificial fermentation processes are clearly separated from the samples points of the spontaneous fermentation process.

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P-FA-26

PECTIN ANALYSIS BY HIGH-PERFORMANCE SIZE-EXCLUSION CHROMATOGRAPHY USING EVAPORATIVE LIGHT SCATTERING DETECTION (HP-SEC-ELSD)

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Pectin is a generic term for some complex materials occurring in the cell wall of plants that can be isolated and used as a technological ingredient for huge number applications in pharmacy and, mainly, in the food industry. Basically, it is a α(1→4) linked polymer of galacturonic acid (GalA), namely homogalacturonan domain, esterified with methanol at some of its 6-C carboxylate groups and with acetic acid to some C-2 and C-3 hydroxyl groups. This chain together with other domains with rhamnose and GalA branched with arabinogalactan and other odd carbohydrates constitute the complex structure of pectin, which strongly affect its functionality. In spite of the more than 180 years of pectin research, a renewed interest toward this polysaccharide has emerged due to the fact that new extraction processes and sources used for its obtainment may afford new structures and properties. One of the main targets is the development of robust analytical methodology which provides new insight in the macromolecular buildup of the pectin polymer [1]. Among the different parameters M_w is particularly important for the characterization of modified pectin. To date, most of the methods are based on the separation by High-Performance Size-Exclusion Chromatography (HP-SEC) using refractive index detector (RID), however, its relatively low sensitivity, dependence of response on temperature and flow rate and inability to be used under gradient elution [2] have focused attention toward the use of the Evaporative Light Scattering Detector (ELSD). It can detect any analyte less volatile than the mobile phase and is a good alternative that improves detection sensitivity and baseline stability [3]. Cameron et al. [4] utilized HPLC-SEC to estimate the M_w of GalA oligomers and Condezo-Hoyos et al. [5] for apple pectin of 140 kDa. In this work, a comparative study using HP-SEC with RID or ELSD as detection systems was carried out for the analysis of the M_w distribution of citrus and apple pectin. An optimization of ELSD conditions by CCD provided 85 and 75 °C as evaporator and nebulizer temperatures and 1.2 mL min^{-1} as flow rate of air. The regression curves were constructed with pullulans (10-2500 mg L^{-1}, 0.342-805 kDa) obtaining coefficients of determination (R^2) of 1 and 0.9804 for quadratic and linear fits, respectively. Detection and quantitation limits were 19.9 and 25.7 mg L^{-1} for quadratic fit and 6.7 and 16.5 mg L^{-1} for the linear one; these limits being 30 and 100 mg L^{-1} for RID. The precision of ELSD and RID systems, evaluated in different days, was 9.4% and 6.5%, respectively. These results demonstrated the suitability of the chromatographic separation here used coupled with ELSD for the analysis of pectin with M_w values close to 700 kDa.

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P-FA-27

USE OF ONION EXTRACT AS DAIRY CATTLE FEED SUPPLEMENT: MONITORING OF PTSO AS MARKER OF ITS EFFECT ON MILK ATTRIBUTES

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The reduction of enteric methane production in ruminants represents both an environmental and a nutritional interest. The most promising strategy is the development of new feed additives that act as rumen modifiers [1]. In this sense, onion extract (OE) has been proposed as feed supplement for dairy cow diet, since it acts as an inhibitor of methane production [2]. Typical properties of OE (odor, flavor and pungency) could influence on milk sensory attributes, which can be negative for its quality. Considering that, analytical methodologies are needed in order to check this possible effect.

In this communication, we propose a strategy to probe that OE does not have any incidence on organoleptic properties of milk. Firstly, a HPLC-UV method has been developed for monitoring propyl propane thiosulfonate (PTSO) as marker of OE. PTSO is an organosulfur compound characteristics of allium genus that has already been determined in feed enriched with OE [3,4]. Also, a rapid sample treatment based on a QuEChERS procedure was proposed for PTSO extraction from milk samples. The method was fully characterized for milk from different ruminants in terms of performance characteristics.

Moreover, a field trial was performed: a livestock consisted on 100 cows which ingested 25 g/day of commercial OE containing PTSO (Garlicon®) for two months (G_1) and 100 cows as control group (C_0) were studied, milk sampling from each group was carried out weekly. The proposed HPLC-UV method was applied for the monitoring of PTSO residues in milk from G_1 and no positive results were obtained above LODs. In order to confirm the results, the samples were submitted to an UHPLC-MS/MS method, previously developed in our lab [4] and considering the higher sensitivity of this technique, small traces of PTSO were detected in the studied milk samples. Samples from G_1 and C_0 were sensorially evaluated by a tasting panel (triangle test), in order to check if milk from G_1 preserved its sensory attributes. The test was performed according to the conditions described in the general guidance ISO 8589:2007 and the design and analysis of sensory discrimination tests was carried out using XLSTAT software. So, although PTSO residue was detected in the studied milk samples from G_1, its concentration does not alter the organoleptic properties. As conclusion we propose Garlicon® to be used as supplement feed at least at the studied dose without any compromise of the milk organoleptic properties, achieving a reduction in the methane emissions.

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P-FA-28

METHOD DEVELOPMENT FOR ERGOT ALKALOIDS IN CEREAL SAMPLES

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The European Food Safety Authority (EFSA) was asked by the European Commission to deliver a scientific opinion on ergot alkaloids (EAs) in food and feed in 2012. The Commission regulation (EU) 2015⁄1940 of 28 October 2015 strongly recommended to monitor the presence of ergot alkaloids in cereals and cereals products and to communicate to EFSA findings on ergot alkaloids including occurrence data and specific information on the relationship between the presence of ergot sclerotia and the level of individual ergot alkaloids. Appropriate and achievable maximum levels, providing a high level of human health protection, shall be considered for cereal and cereal products before 1 July 2017.

An ultra-high liquid chromatography–tandem mass spectrometry (LC–MS/MS) method is developed for the determination of ergot alkaloids in cereal matrix. The method allows the simultaneous analysis for 8 different ergot alkaloids: Ergocornine, Ergocristine, Ergocryptine, Ergosine and their corresponding epimers.

Chromatographic conditions have been optimized using:

1) 7 different chromatographic columns
2) Formic acid or ammonium hydroxide as aqueous phase
3) Acetonitrile or methanol as the organic phase.

Regarding the detection method, MRM has been obtained for each compound optimizing every step of the detection process.

A sample of a mixture of five precooked ecological whole grain flakes of oats, wheat, rye, barley and corn has been analyzed.

Different sample prep methods have been studied for cereal matrix including solid-liquid extraction, concentration-reconstitution, defatting processes, QuEChERS and SPE cartridges.

High-Res QTOF system has also been used in order to compare selectivity and sensitivity.

P-FA-29

Study of volatile organic compounds in hydroalcoholic samples by SPME-GC-FID

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The Solid-phase microextraction (SPME) is a technique with a great adsorption capacity and high selectivity, without solvent requirement. For this reason, this technique is considered suitable for analyze volatile organic compounds in hydroalcoholic solutions, such as wine samples, which contain a broad variety of volatile organic compounds in low concentration levels.

In the present study it has been optimized a method for determining volatile organic compounds in a hydroalcoholic solution by SPME and analysis by Gas Chromatography with Flame Ionization Detector (GC-FID).

In the extraction step by SPME it has been studied the influence of sample volume, sodium chloride addition, temperature and type of fiber used. The desorption step has been carried out with a Split/Splitless injector. It has been considered the following injection parameters: mode (Split/Splitless, standard or Pulsed), temperature, type of glass liner, pressure, split ratio and septum purge flow.

Once the method has been optimized, it has been demonstrated its linearity, repeatability, accuracy, limit of detection and limit of quantification. Furthermore, the optimized procedure has been applied to a spiked wine sample to study the wine matrix effect over volatile organic compounds.

Finally, SPME-GC-FID developed procedure has allowed to estimate equilibrium constants (liquid-gas, gas-fiber and liquid-fiber) and volatile organic compounds distribution between different phases.

P-FA-30

DETERMINATION OF AMINOGLYCOSIDES IN MILK AND MILK-BASED FUNCTIONAL FOODS BY HILIC-BASED UHPLC-MS/MS AND MOLECULARLY IMPRINTED POLYMER SOLID PHASE EXTRACTION

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Veterinary use of antibiotics is controlled by Regulation (EU) No 37/2010 and maximum residue limits (MRLs) have been established in the case of milk. Aminoglycosides (AGs), used for the treatment of animals bred for meat and milk production, require an effective method for the monitoring of their residues in these commodities. AGs are very hydrophilic compounds and are difficult to retain on conventional reverse stationary phase columns. Hydrophilic interaction liquid chromatography (HILIC) provides an alternative approach to effectively separate small polar compounds on polar stationary phases. In this work we have established a HILIC-based UHPLC-MS/MS method for the determination of eleven AGs (gentamicin C1, gentamicin C1a, gentamicin C2, apramycin, paromomycin, dihydrostreptomycin, pectinomycin, kanamycin, lincomycin, amikacin, tobramycin and streptomycin) using a HILIC column (Kinetex, 50 mm × 2.1 mm, 1.8 µm). Under optimum conditions, the separation of AGs was achieved in less than 3 min, with a mobile phase consisting of 150 mM ammonium acetate containing 1% formic acid (solvent A) and MeCN (solvent B) at a flow rate of 0.5 mL min^{-1} and 35 °C. The analytes were detected in ESI (+) mode with MRM mode and fragmentation conditions were optimized in order to obtain the highest sensitivity. Moreover, a challenge in the monitoring of AGs in highly complicated matrices, such as milk and milk-based preparations, is related with the extraction and cleanup procedure. Molecularly imprinted polymer solid-phase extraction (MISPE) can provide cleaner extracts because the strong and selective interaction between MIPs and target molecules, being of special interest for complex matrices. In this work MISPE has been proposed as sample treatment.

The developed method was validated according to the European Decision 2002/657/EC and was applied to different types of milk (whole cow milk, skimmed cow milk, goat milk) and milk-based functional foods (infant milk, milk enriched with omega-3 and milk enriched with isoflavones). Matrix effects were lower than |15|% in all cases. Limits of quantification, in the range 4.2 – 49 µg kg^{-1}, were lower than the MRLs established for milk. Recoveries ranged from 70– 106% with RSD lower than 13%, being in compliance with the current legislation.

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P-FA-31

DETERMINATION OF ESTROGENIC COMPOUNDS IN DAIRY PRODUCTS USING THE QuEChERS METHOD COMBINED WITH ULTRA HIGH PERFORMANCE LIQUID CHROMATOGRAPHY TANDEM MASS SPECTROMETRY

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Natural estrogens are substances synthesized by the organism that are involved in the development of sexual and reproductive female features of humans and animals [1]. Apart from them, and due to their similarity, there is also an important group of compounds called exoestrogens that can mimic them and act either enhancing or suppressing their activity. Some of these compounds have a synthetic origin while others are produced by a natural source such as myco- and phytoestrogens. These compounds can appear in dairy products increasing the levels of estrogenic activity in the consumers and consequently, producing a large number of endocrine disorders or even cancer in hormone-dependent organs.

The QuEChERS (*quick, easy, cheap, effective, rugged, and safe*) method is one of the most frequently used worldwide, mainly for pesticide residue analysis. In fact, the method is highly used in official laboratories and its application has been extended to the determination of a large number of analytes and commodities due to its simplicity. Besides, QuEChERS has shown great versatility for the combination with diverse analytical techniques [2]. However, and despite the excellent and inherent advantages of the methodology as sample preparation approach, only a few of studies have been developed for the determination of estrogenic compounds in dairy products.

In this work, the QuEChERS method has been combined with ultra-high performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS) for the analysis of 22 estrogenic compounds including four endogenous estrogens (i.e. estrone, estriol, 17α-estradiol and 17β-estradiol), four synthetic (i.e. dienestrol, diethylstilbestrol, hexestrol and 17α-ethynylestradiol), six mycoestrogens (i.e. zearalanone, zearalenone, α-zearalanol, β-zearalanol, α-zearalenol and β-zearalenol) and eight phytoestrogens (i.e. prunetin, biochanin A, daidzein, formononetin, genistein, glycitein, enterolactone and enterodiol) in cheese and kefir samples. The methodology was validated for the different matrices obtaining limits of detection in the low µg/Kg range with recoveries in the range 70-120% and relative standard deviations below 20%.

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P-FA-32

EXTRACTION AND CHARACTERIZATION OF BIOACTIVE INOSITOLS FROM MUNG BEAN

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Importance of biological activities of carbohydrates is currently increasing in different research areas such as food, pharmaceutical or environmental science. Inositols are cyclic polyalcohols with molecular formula $C_6H_{12}O_6$ which exhibit different activities mainly related to insulin resistance [1]. *Myo*- and *chiro*-inositol are the most abundant inositols in nature but methyl-inositols, glycosyl-inositols and glycosyl-methyl-inositols are also widespread in the vegetal kingdom.

Chemical synthesis has been used for the production of inositols, although this process is still expensive. Consequently, the extraction of these compounds from natural sources using more economical and less time consuming procedures is attracting great interest from the food industry with the intention of incorporating them as bioactive food ingredients.

It is well known that cyclitols are found in legumes such as chickpea, lentil, adzuki bean or grasspea [1]. Mung bean (*Vigna radiata*) is an important foodstuff in China, India and Bangladesh but scarce information about their cyclitol composition is available [2].

Therefore, the aim of this work was to exhaustively characterize the inositols present in mung beans and to optimise a method for the obtainment of bioactive cyclitol enriched extracts. As a first approach, the extraction procedure was optimized using various solvents (water, methanol and ethanol) and different conditions (temperature and time). Carbohydrates, previously derivatized to their trimethylsilyl oximes, were analysed by GC-MS using a 5% phenyl polycarborane-siloxane column.

Apart from saccharides such as fructose, glucose and sucrose, *scyllo*-, *myo*- and methyl-*scyllo*-inositol were detected. Moreover, several peaks with mass spectra compatible with glycosyl-cyclitol structures (derivatives of inositols and methyl-inositols not previously described) were found. Regarding the extraction method, the best cyclitol yields were achieved using water as extractive solvent; however, high concentrations of other sugars which could interfere in their bioactive properties were also obtained. Alcohols were more selective solvents for the extraction of cyclitols, but yields were very low. Finally, a mixture of water:ethanol (50:50, v:v) was the most appropriate solvent, obtaining acceptable cyclitol yields with a low contribution of interfering sugars.

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P-FA-33

DEVELOPMENT OF A GREEN MICROWAVE-ASSISTED EXTRACTION METHOD TO OBTAIN MULTIFUNCTIONAL EXTRACTS OF *MENTHA* SP.

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Nowadays, there is a large body of evidence supporting plant extracts as a natural source of bioactives. However, the exploitation of plant bioactives requires the previous selection and optimization of the most appropriate extraction technique in terms of both extraction yield and bioactivity. The genus *Mentha* L. has been described to possess a number of biological activities including antioxidant and antimicrobial [1]. Among other advanced extraction techniques, Microwave Assisted Extraction (MAE) has been reported as advantageous for the extraction of plant bioactives as it provides a quick heating and improved yield. However, this technique has scarcely been applied to obtain *Mentha* sp. bioactives [2].

In the present study, a new MAE method has been developed to obtain multifunctional extracts from *Mentha* sp. Optimization of MAE process was done with *M. rotundifolia* (L.) Huds.: first, the best extraction solvent (water, methanol, ethanol and acetone) was selected; second, extraction temperature (50-100 °C) and time (5-30 min) were evaluated. Optimal conditions were chosen to maximize the bioactivity of extracts. Antioxidant activity was determined by the total phenolic content (TPC) and DPPH assays. Antimicrobial and antifungal activities were evaluated by the agar disc diffusion method against Gram (+) bacteria (*S. aureus, L. monocytogenes*), Gram (-) bacteria (*E. coli*, *S. typhymurium*) and fungi (*C. Albicans*). The fully optimized method was further applied for the extraction of different *Mentha* species. MAE extracts were fully characterized by Gas Chromatography coupled to Mass Spectrometry (GC-MS), after the required derivatization process, using a 5% phenylmethylsiloxane column, and by Liquid Chromatography-Mass Spectrometry (LC-MS), using a C18 reverse phase column and a binary gradient.

Antioxidant activity of MAE extracts decreased in the following order: acetone <ethanol<methanol<water. Furthermore, water extracts were the only active against *S. aureus*. 100°C and 17.5 min provided the highest antioxidant activity (TPC: 37.21 mg mL^{-1} GAE; DPPH: 56.13 µg mL^{-1} Trolox) and the highest halo of growth inhibition (1.7 mm diameter) of this bacteria. Derivatized MAE extracts analyzed by GC-MS were characterized by a number of carbohydrates (glucose, fructose, sucrose, etc). Different phenolic acids (rosmarinic, caffeic, etc) and flavonoids (luteolin) were also determined by LC-MS, their quantitative values being dependent on the species considered.

As conclusion, the MAE method here optimized has been shown as a promising green and efficient procedure for obtaining multifunctional extracts of *Mentha* sp. for their further application as functional ingredients and/or natural preservatives in the food industry.

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P-FA-34

CAPILLARY ZONE ELECTROPHORESIS COUPLED WITH QUADRUPOLE-TIME-OF-FLIGHT MASS SPECTROMETRY FOR THE DETERMINATION OF QUINOLONES AND TETRACYCLINES IN MILK SAMPLES

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Quinolones (Qns) and Tetracyclines (TCs) are widely used in human and veterinary medicine. Extensive use of these antibiotics in veterinary medicine and medicated feed plays a crucial role in intensive production of animals bred for food. This leads to a significant increase in antibiotic resistance and allergic reactions, having therefore important consequences for public health. The European Union has set maximum residue limits (MRLs) of antibiotics in foodstuffs of animal origin as milk by means of Commission Regulation N.37/2010.

In this work we propose a new analytical method based on capillary zone electrophoresis-tandem mass spectrometry (CZE-MS/MS) for the identification and simultaneous quantification of fifteen antibiotics (7 Qns and 8 TCs) in milk samples. Detection using an Accurate-Mass Quadrupole Time-of-Flight (Q-TOF) was used. Thus, the unequivocal confirmation according to the most stringent EU criteria was possible. The main advantage of Q-TOF MS is the availability of full MS/MS spectra after a single injection for identification and confirmation purposes. In addition, a solid-phase extraction (SPE) method using the new HLB Prime cartridge was applied for cleanup. This sorbent allows avoiding the tedious steps such as conditioning, equilibrating and washing. Thus, the sample throughput is higher than when using the conventional HLB technology. The method was optimized and validated using whole cow milk as representative matrix. Good linearity was obtained ($R^2 > 0.992$) for all the studied antibiotics. The precision (intra- and inter-day), expressed as relative standard deviation (%, RSD), at two concentration levels (50 and 100 µg kg^{-1}) was below 13%. Recoveries obtained from goat milk, whole, and semi-skimmed cow milk, at two concentration levels, ranged from 76 to 106%. The limits of quantification ranged from 1.5 to 9.6 µg kg^{-1}, being lower than the corresponding MRLs. Thus, the proposed SPE-CZE-Q-TOF-MS/MS is suitable for monitoring these residues in different types of milk samples.

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P-FA-35

INFLUENCE OF PHENYLALANINE AND UREA APPLICATION AT TWO DOSES TO GRAPEVINE LEAVES ON GRAPE VOLATILE COMPOSITION

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Nitrogen is one of the fundamental elements for the plant, because it promotes its growth and vigor [1]. Moreover, this element is directly involved in the growth of yeasts during fermentation, may even cause sluggish or stuck fermentations [2], so that nitrogen fertilization is important to ensure growth of the vine and a correct composition of the grape and wine. Currently, there are new fertilization techniques such as foliar fertilization, due to assimilation fast and efficient way of products applied to plants [3]. Grape aroma consists of several hundred volatile compounds belonging to different chemical families, being the most important terpenes, C_{13} norisoprenoids, benzenoids, esters, and C6 compounds. The aim of this work was to study the effect of foliar application of phenylalanine and urea, at two different doses, on the aromatic grape composition.

Therefore, to carry out the foliar treatments, aqueous solutions were prepared with the corresponding concentration of phenylalanine (Phe), and urea (Ur). Control plants were sprayed with water solution. The treatments were applied to grapevine twice, at veraison and one week later. The total amount applied in each treatment was 0.9 kg N/ha for Phe1 and Ur1 and 1.5 kg N/ha for Phe2 and Ur2. Treatments were carried out in triplicate. Grapes were analyzed by HS-SPME-GC-MS in order to determine their volatile composition [4].

The results showed that phenylalanine treatment at low dose as nitrogen source improved the presence of esters and benzenoids, decreased the content of terpenoids and C6 compounds, while its effect on C_{13} norisoprenoids did not show a clear trend. For the urea treatment at low dose the content of all compounds increased, except C6 compounds. The same happened when the highest dose of phenylalanine was applied, showing that the presence of all compounds increased in the grapes, except C6 compounds. For the higher dose of urea, the content of terpenenoids, C_{13} norisoprenoids and esters increased while benzenoids and C6 compounds decreased. Consequently, the best results were obtained when the highest doses of both nitrogen sources were used, being urea the best treatment to improve the grape aromatic composition.

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P-FA-36

NANOFLOW LIQUID CHROMATOGRAPHY HIGH RESOLUTION MASS SPECTROMETRY FOR MULTI-RESIDUE ANALYSIS OF VETERINARY DRUGS IN FOOD SAMPLES OF ANIMAL ORIGIN

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The presence of veterinary drugs residues in the food chain is of increasing concern provided the adverse effect for human health, such as allergic reactions and the possible development of antibiotic bacterial resistance. For this reason, the European Union (EU) has established a maximum residue limit (MRL) for some antibiotics in foods from animal origin. Downsizing the flow stream in liquid chromatography electrospray tandem MS has been proven to be an interesting alternative to standard analytical size approaches, provided the significant benefits in terms of sensitivity and matrix effect reduction. In this sense, the use of nanoflow liquid chromatography coupled to nanospray MS detection has been restricted so far to selected bioanalytical applications (eg. proteomics). The introduction of more robust and reproducible ultra-high pressure nanoflow LC instrumentation along with new column technology integrating the nanospray spray emitter and the column in a single item, has made accessible such sophisticated approach to routine work, avoiding typical nanoflow operation issues. In this work, a nanoflow LC-MS method has been developed for the multiresidue determination of veterinary drugs in different food matrices. A Thermo Scientific EASY-nLC 1000 nano-LC system was used. An EASY-Spray column (PepMap®, C18, 3 µm, 100Å, 75 µm x 150 mm) was employed. Mobile phases A and B were water and acetonitrile, respectively, both with 0.1 % formic acid. The injection volume was 1 µL. Flow rate was set at 300 $nL \cdot min^{-1}$. A Thermo Q-Exactive Orbitrap mass spectrometer equipped with an Easy-Spray nano-electrospray ion source was used. Q-Exactive was operated in all ion fragmentation and full scan modes. The proposed method was applied to the determination of veterinary drugs in food samples such as milk, honey, egg and beef. Salting-out supported liquid extraction was selected as sample treatment. From the results obtained, the sensitivity achieved with this configuration enables the implementation of high dilution factors (1:50) in veterinary drug residue workflows without compromising sensitivity and yet, performing limit of quantitation (LOQ) between 0.03 to 3000 ng Kg^{-1}. These LOQs were significantly lower than their corresponding MRL set. The precision was also evaluated, obtaining RSD values lower than 20% in all cases.

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P-FA-37

DEVELOPMENT OF A POLYMERIC SORBENT MODIFIED WITH GOLD NANOPARTICLES FOR SOLID PHASE EXTRACTION OF HUMAN MILK WHEY PROTEINS

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Nutritional composition of human milk as well as its non-nutritive bioactive factors are considered essential to promote young infants with a healthy growth and development. In this sense, protein fraction in milk particularly provides beneficial outcomes in breast-feeding. The variety of proteins contained in human milk is wide. These include the caseins (ß-casein, κ-casein, αs1-casein) and whey proteins such as α-lactalbumin (α-La), lactoferrin (Lf), immunoglobulins (sIgA, IgM, IgG), serum albumin (HSA), and lysozyme (Lyz). In human milk, the whey fraction contains the majority of the protein (80% in early lactation and 60% in mature milk), whereas caseins represent a smaller fraction. The separation of human milk casein is usually carried out through precipitation at its isoelectric point (pH 4.6). However, rapid and direct isolation of human milk whey proteins without prior precipitation of caseins has not been reported to date. For these reason, a relative simple method to allow rapid analysis of the major whey proteins in human milk might be of interest for further characterizations.

In this work, a solid-phase extraction (SPE) sorbent based on the modification of a polymeric material with gold nanoparticles (AuNPs) has been developed and applied to the isolation of human milk whey proteins. The conditions for the extraction and elution of whey proteins (α-La, HSA, Lf and Lyz) onto this support have been explored. Loading capacity and regenerative ability of the SPE polymeric material was also evaluated. The ability of the developed sorbent to isolate human milk whey proteins was tested following two approaches: with and without prior extraction of target proteins. This work represents the first application of SPE sorbents modified with AuNPs for the direct extraction of human milk whey proteins with a simple sample dilution.

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P-CPA-1

ANALYSIS OF PROSTATE SPECIFIC ANTIGEN (PSA) BY CAPILLARY ELECTROPHORESIS AND TWO-DIMENSIONAL GEL ELECTROPHORESIS. COMPARISON AND COMPLEMENTARITY

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The prostate cancer (PCa) biomarker usually employed in clinics is the serum concentration of prostate specific antigen (PSA). However, PSA is an organ-specific but not a cancer-specific glycoprotein and PSA level in serum is also elevated in non-malignant conditions of the prostate, such as benign prostatic hyperplasia (BPH). On the other hand, it is known that cancer can modify glycosylation of proteins. Thus, several efforts are focused on the search of alternatives to improve PCa diagnosis through the study of PSA subforms that could be cancer associated, such as PSA glycoforms, as we have recently shown [1].

By using two dimensional gel electrophoresis (2DE) we have previously observed a decrease in the sialic acid content of PSA from PCa compared to BPH patients, based on the different proportion of the PSA spots with different sialic acid content [2,3]. However, analytical techniques which are faster, more quantitative, and easier to automate than 2DE are desirable.

In this study we have examined the potential of capillary electrophoresis (CE) for resolving PSA subforms in different samples and have compared the results with those obtained by 2DE.

To do so, we have carried out the following experiments: First, we have performed OFFGEL-fractionation of standard PSA from seminal plasma according to their pI and have analyzed each separated fraction by 2DE and CE. Second, commercial non-fractionated PSA and high pI PSA have been analyzed by both techniques. Finally, we have compared the 2DE and the CE patterns of PSA from seminal plasma from healthy donors and from urine of a PCa patient.

Along the study, we have observed that different samples which present different PSA spots proportions by 2DE, have different CE profiles as well. As a result of the study, a tentative correspondence between 2DE spots and CE peaks has been established and it is concluded that CE is a useful and complementary technique to 2DE for the analysis of samples with different PSA subforms, which can be of high interest in a near future for studying relevant clinical samples.

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P-CPA-2

ANALYTICAL STRATEGIES TO INVESTIGATE NPS IN LEGAL HIGHS

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The increase in the number, type, and availability of new psychoactive substances (NPSs) with possible health and social risk is of alarming concern. NPSs, intended as legal replacements of conventional illicit drugs, usually have minor modifications to the backbone structure of existing substances. In 2014, 101 NPSs were detected in the European Union for the first time according to EMCDDA data. Thus, a good analytical strategy is needed for the detection and identification of NPSs. Additionally, the absence of reference standards renders this task increasingly challenging. For these reasons, a combination of spectroscopic and mass spectrometric techniques is required for a true confirmation of the identity.

In this work, we described the structure elucidation strategy used at our laboratory for identification and characterization of NPS in legal high samples. Thus, analysis of the samples is undertaken using GC–MS, UHPLC–QTOF-MS, NMR, and finally, if necessary X-ray crystallography. This work shows the advantages and limitations of these techniques, with several illustrative examples.

Initially, samples were analyzed by GC(EI)–MS, which resulted useful when the compounds were included in commercial or free standardized libraries. However, due to the novelty of NPS which are continuously changing, they are not typically included in existing libraries. Therefore, although for most of compounds no definitive information was obtained, some structural information was gained.

For structure elucidation additional analyses were necessary. In the case of UHPLC-QTOF MS, the presence of the (de)protonated molecule was searched in the samples by performing automated exact mass ion chromatograms for all compounds included in a home-made database containing around 1000 NPS. After that, fragment ions, typically in the HE function, and characteristic isotopic ions were further evaluated. However, in most situations more than one candidate for each detected peak was proposed, due to the high number of isomeric/isobaric compounds included in the database. Obviously, this fact complicated the elucidation process. In this case, the evaluation of the fragment ions observed, allowed reducing the number of candidates. When available, the tentative identification of compounds detected was supported by MS/MS product ions reported in the literature for the suspect compound (either in exact or nominal mass). Finally, when fragmentation was not conclusive (especially in the case of positional isomers), additional experiments were performed using NMR (^{1}H NMR, ^{19}F NMR, ^{1}H-^{13}C heteronuclear quantum coherence and 1H-1H correlation spectroscopy). In some exceptional cases, i.e., when no candidate was found, X-ray crystallography was needed for structural elucidation.

P-CPA-3

IS DEPROTEINIZATION NECESSARY IN THE DETERMINATION OF HUMAN PLASMATIC STEROIDS BY GC/IT-MS/MS ANALYSIS?

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For many years concentrations of functional steroid hormones or their precursors have been determined mainly in plasma or serum samples of patients, occasionally in saliva or tissues, or as their metabolites, in urine or amniotic fluid.

Bibliography shows that protein precipitation for human plasma analysis performed by GC/MS can be performed successfully with methanol by centrifugation with acetonitrile with 70% perchloric acid and n-hexane , with 5% sulfosalicylic, with ethanol , with acetone, and with trichloroacetic acid . Other methods for plasma deproteinization focus on physical methods as described. These methods include ultrafiltration and centrifugation with varied molecular weight cut-offs, or using other simple methods such as heating the plasma. However, it has not been shown that these deproteinization methods interfere with gaschromatography-ion trap-tandem mass spectrometry (GC/IT-MS/MS) analysis of plasmatic steroids.

Hence, the aim of this work was to identify if it is necessary and useful to apply a deproteinization treatment to human plasma before its analysis in order to determine steroids hormones using GC/IT-MS/MS.

In this work, we have performed several deproteinization tests with acetonitrile, methanol, ethanol, HCl 0.5 M/methanol (1:1) (v/v), trichloroacetic acid (10%), sulfosalicylic acid (20%) and perchloric acid, proteases and activated carbon before analyzing twelve plasmatic steroids hormones using gas chromatography directly coupled ion-trap mass spectrometry.

Signal/noise ratios of tests were determine to assess whether a previous deproteinization treatment is necessary or not prior to their analysis. The use of chemical deproteinization methods, proteases and active carbon did not improve the signal/noise ratio.

Deproteinization is not required for the analysis of steroid hormones in plasma using gas chromatography-directly coupled ion-trap mass spectrometry.

P-CPA-4

COMPARISON OF CHROMATOGRAPHIC PROFILES FROM ELECTROCHEMICAL AND IN VITRO ASSAYS FOR THE ASSESSMENT OF DRUG METABOLISM

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The identification of the metabolites generated in the organism is an important task in drug discovery and development. During the early stages of discovery, the identification of metabolites can be used to define the most proper strategy for leading to optimization, adjusting metabolic clearance and minimizing bioactivation. Hence, an early assessment of the metabolite profile may be critical since metabolites can contribute to pharmacological and/or toxicological effects.

The so-called biomimetic strategies have recently been proposed as a complement to conventional *in vitro* and *in vivo* assays to assess the drug metabolism in a simpler and faster way. Among other possibilities, the electrochemical (EC) generation of metabolites has been found to be highly promising for high-throughput screening, especially for dealing with reactive metabolites [1].

In this study, the EC metabolite generation is proposed as an alternative method to simulate the oxidative drug metabolism based on liver microsome assays. Various commercial drugs belonging to different therapeutic families have been explored as a model to compare the metabolic behavior from both *in vitro* and EC approaches. Drugs have been selected to cover different metabolism extents, from those highly metabolised to unaltered ones, as well as a wide variety of biotransformations such as *N*-dealkylation, *S*-oxidation, dehydrogenation and hydroxylation reactions. The resulting samples have been analyzed by liquid chromatography with UV detector (HPLC-UV). For such a purpose, specific HPLC methods for each drug and its metabolites have been stablished based on reversed phase mode (Kinetex C_{18} column, 100 mm × 4.6 mm i.d., particle size 2.6 µm). Elution gradients have been optimized using 0.1% (v/v) formic acid aqueous solution and MeOH as the components of the mobile phase.

Drug metabolite profiles from both EC- and microsome-based methodologies have been compared in terms of variety, proportion and extent of total transformations. In general, most of the metabolites occurring *in vitro* have also been detected in the EC runs. Besides, it has been found that compositional profiles from EC experiments are dependent on experimental variables such as pH and potential, so working conditions can be tuned to try to reproduce the *in vitro* results as much as possible.

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P-CPA-5

DEVELOPMENT OF SIMPLE ISOCRATIC HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY ANALYTICAL METHOD FOR DETERMINATION OF PHYTOSTEROLS AND CHOLESTEROL IN PARENTERAL LIPID EMULSIONS

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Introduction: Determination of phytosterols and cholesterol has an increasing clinical importance. However, the majority of available analytical methods allow the separation of only few phytosterols and under complex chromatographic conditions.

Objective: Develop a single high pressure liquid chromatography (HPLC) analytical method with simple chromatographic conditions for qualitative and quantitative determination of phytosterols and cholesterol.

Materials and methods: A mixture of sterol standards (beta-sitosterol, brassicasterol, campesterol, cholesterol, desmosterol, ergosterol, lanosterol, lathosterol, stigmasterol) was dissolved in methanol and analysed with HPLC chromatograph Dionex UltiMate 3000, equipped with pump (LPG–3400 M), autosampler (WPS3000) and detector (PDA-3000). Isocratic analysis with several mobile phase mixtures of acetonitrile (ACN), methanol (MeOH) and water (H_2O) was performed on column C18 (Symmetry C18, 150x3,9 mm, 5µm, Waters), column Phenyl (Zorbax SB-Phenyl, 150x4,6 mm, 5µm, Agilent) and column C8 (Zorbax XDB-C8, 150x4,6 mm, 5µm, Agilent). Flow varied from 1,0 to 2,0 mL/min. Injection volume was 10 µL. Column temperature was maintained at 30°C and detection was set at 210 nm.

Results: For each column optimal isocratic conditions were established. Column C18 had the shortest time of analysis (30 min) and the simplest mobile phase mixture (ACN/MeOH = 98:2). However, there was present campesterol and stigmasterol peak overlapping due to hydrophobic interactions.

Analysis with column Phenyl lasted 45 min and required more complex mobile phase mixture (ACN/MeOH/H_2O = 48:22,5:29,5). Change in column chemistry resulted in campesterol and stigmasterol separation, however, lanosterol and stigmasterol coeluted.

Separation of all sterols in prepared standard solution was achieved with column C8 in 45 min and mobile phase mixture ACN/MeOH/H_2O = 80:0,5:19,5.

Conclusions: The proposed analytical method is the first method that successfully separates all 9 sterols, with similar chemical structure, in a single RP-HPLC analysis, under simple chromatographic conditions, using C8 column and mixture of ACN/MeOH/H_2O as mobile phase.

P-CPA-6

ANALYSIS OF BASIC DRUGS IN PHARMACEUTICAL FORMULATIONS USING LIQUID CHROMATOGRAPHY WITH WATER AND DETERGENT

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Micellar liquid chromatography (MLC) was first proposed as a "green" chromatographic mode, using mobile phases of water and surfactant (detergent) without organic solvent. However, in most reported procedures, which employ sodium dodecyl sulphate (SDS) as surfactant, a small amount of organic solvent is required to decrease the retention of analytes to adequate values. Moreover, in the separation of basic compounds, such as β-blockers, the attraction of the cationic species to the stationary phase modified with the anionic surfactant demands the addition of a relatively high amount of propanol or acetonitrile, or even a more hydrophobic alcohol to increase the elution strength of the mobile phase. Recently, mixed micellar mobile phases prepared with both SDS and the non-ionic surfactant Brij-35 have demonstrated to modulate the retention of β-blockers to appropriate times, which eliminates the need of an organic solvent. In this work, we show that this approach can be applied to develop a "green" method to determine β-blockers in pharmaceutical formulations. The use of an organic solvent is thus avoided throughout the whole analysis. The results are compared with those obtained using a micellar mobile phase containing SDS and propanol. By performing an extensive validation, the stationary phase performance was checked to be maintained at least during several weeks, after elution with mixed micellar mobile phases of SDS and Brij-35.

P-CPA-7

DYNAMIC CHANGES IN THE COMPOSITION OF THE CENTRAL NERVOUS SYSTEM MYELIN. STUDY AT DIFFERENT ADULT AGES BY LIQUID CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY

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Sulfatides are amphiphilic molecules that contain a polar head –namely, a galactose residue with a sulfate group at position 3, bound to a ceramide moiety via a glycosidic linkage-, and they are found on the extracellular leaflet of the myelin. Changes in sulfatide levels have been associated with the pathogenesis of different human CNS diseases, including multiple sclerosis, Parkinson's disease, leukodystrophy and Alzheimer's disease. These studies have pointed out that sulfatides can be potentially used as biomarkers in neurological diseases. Moreover, the composition ratio among the different sulfatide species has been related to human and mouse brain changes during normal ageing.

Recently, we have developed a new liquid chromatography-tandem mass spectrometry method using a quadrupole-time of flight analyzer and electrospray ionization, working in the positive ionization mode (LC-ESI(+)-MS/MS), to profile the sulfatide content in biological samples. In order to evaluate its reliability, we have applied this method on myelin isolated from adult mice at different ages (from postnatal 60 days, and at successively older stages, i.e., 120, 240 and 365 days), which reflect lifespan dynamics changes on the composition of myelin also in maturity-adulthood.

Using the ESI(+)-MS/MS fragmentation patterns and the accurate mass values, it was possible to identify and quantify 37 sulfatides in myelin from mouse brain, including molecules with different fatty acid chain length as well as degree of unsaturation and hydroxylation. A chemometric analysis of their relative abundances revealed that sulfatides with odd-numbered fatty acid chains undergo the greatest and a more systematic increase with age. A rise in hydroxylated species was also found at the most advanced age. The results obtained show that the developed method can be a very useful tool in the field of bioanalysis, due to its ability to detect and correctly identify these potential biomarkers at very low concentrations.

The good results obtained, in agreement with the literature data, indicate that the method that we developed here may be particularly helpful whenever a correct discrimination among different types of sulfatides is necessary.

P-CPA-8

A NEW LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY METHOD FOR SULFATIDES SCREENING BASED ON THE WRONG-WAY-ROUND ELECTROSPRAY IONIZATION EFFECT

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Myelin is the insulating sheath around axons, which is essential for high-speed transmission of electrical impulses and providing trophic support to axons. In the Central Nervous System (CNS), the only myelin-forming cells are oligodendrocytes. The CNS myelin is rich in lipids, mainly cholesterol, galactosylceramide and sulfatides. Among the latter, the glycolipid sulfatides are characterized by an amphiphilic molecule, which contains a polar head: namely, a galactose residue with a sulfate group at position 3, bound to a ceramide moiety via a glycosidic linkage. Sulfatide composition is very complex, as there are many species with different length, as well as degree of unsaturation and/or hydroxylation of their fatty acyl chain. Due to this complexity, the analytical technique of choice to characterize these compounds has been liquid chromatography coupled to mass spectrometry, mainly with triple quadrupole analyzers and electrospray ionization working in the negative mode (LC-ESI(-)-MS/MS). However, the number of sulfatides detected is usually scarce, such that sometimes confidence in their identity is limited, mainly because of the poor structural information obtained from the negative tandem mass spectra.

Thus, taking these limitations into account, we have developed a new high-performance liquid chromatography-mass spectrometry method capable of carrying out a comprehensive and reliable sulfatide profiling in biological samples. This method is based on obtaining quasimolecular wrong-way-round ions by positive electrospray ionization, then recording the precursor and product mass spectra in the high resolution accurate-mass mode. The applicability and qualitative performance of the developed method was confirmed using myelin samples isolated from adult mice.

The LC-ESI(+)-MS/MS method used an acetonitrile/water gradient on an octadecylsilane column at 45 °C, and 5 mM of ammonium acetate at pH = 4.5 as modifier. Surprisingly, very intense and informative diagnostic ions in the MS/MS spectra were obtained when working in the positive ESI mode, due to a 'wrong-way-round' ionization effect. This effect, which has not been previously described for this type of molecule, has made it possible to correctly identify sulfatides, even at very low concentrations.

P-CPA-9

STRATEGIES FOR THE DETECTION OF NEW BISGLUCURONIDE, DIGLUCURONIDES AND DICONJUGATED METABOLITES OF ANABOLIC ANDROGENIC STEROIDS

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Anabolic androgenic steroids (AAS) are the substances most frequently detected in doping control analyses. Most AAS are extensively metabolized and excreted in urine mainly as phase II metabolites, however most of the metabolic profile remains unknown. Previous studies on phase II metabolism of AAS were based on enzymatic hydrolysis with β-glucuronidase and only unconjugated and glucuronides hydrolysable under these conditions were detected. Other phase II metabolites not systematically studied for AAS are bisglucuronides, diglucuronides and diconjugates. Liquid chromatography-mass spectrometry (LC-MS) allows for the direct analysis of steroid conjugates such as glucuronides resistant to enzimatic hydrolysis, sulfates or conjugates with cysteine.

The objective of this work was to study new conjugated metabolites (bisglucuronide, diglucuronide and diconjugated) of AAS by LC-MS/MS in urine samples.

In the case of AAS bisglucuronides, several compounds were synthesized and, the ionization and CID behavior were studied. Bisglucuronides ionized as $[M+NH_4]^+$, $[M-H]^-$ and $[M-2H]^{2-}$. In positive mode, the most common fragments of steroid bisglucuronides were result from the loss of 211, 229, 387 and 405 Da, and the ions at m/z 141, 159 and 177. The CID-spectra of the $[M-H]^-$ ion show only the neutral loss of 176 Da. Fragmentation of $[M-2H]^{2-}$ show ion losses of 175 and 75. The ions at m/z 75, 85 and 113 were also observed in the fragmentation of $[M-H]^-$ and $[M-2H]^{2-}$. For bisconjugates the CID-spectra of the $[M-H]^-$ ion produced the neutral losses of 80, 176 and 256 Da. For diglucuronides, the fragmentation of $[M+NH_4]^+$shows the neutral losses of 352 and 176Da, and the CID-spectra of the $[M-H]^-$ ion show the neutral loss of 176 Da, and the ions of m/z 351, 193 and 175.

The common ionization and fragmentation behavior observed for steroid conjugates will be used as a basis for the development of open scan methods (PI and NL methods) and SRM methods to detect this type of metabolites. Excretion study samples collected after administration of nandrolone, norandrostendiol and testosterone were analysed. Three bisglucuronides and one bisconjugated metabolites were detected in urine samples by SRM strategies.

P-CPA-10

ENANTIOMERIC DETERMINATION OF THE ANTIUREMIC DRUG COLCHICINE BY ELECTROKINETIC CHROMATOGRAPHY WITH ANIONIC CYCLODEXTRINS

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Colchicine ((-)-*N*-[(7*S*)-1,2,3,10-tetramethoxy-9-oxo-5,6,7,9-tetrahydrobenzo[*a*] heptalen-7-yl]acetamide) is a chiral drug obtained from the corm and seeds of the autumn crocus, *Colchicum automnale,* and other Liliaceae. This naturally occurring alkaloid has been used for the treatment of mediterranean fever, cardiac diseases, as specific anti-inflammatory agent in sharp crisis of gout and more recently as an experimental antineoplastic agent [1].

Both enantiomers of colchicine are active but the S-enantiomer was found to be slightly more potent [2]. Since this drug is commercialized as a pure enantiomer, chiral methodologies are needed to ensure its optical purity. These methodologies should separate both enantiomers and also detect low amounts of the enantiomeric impurity.

The enantiomeric separation of colchicine has only been reported by TLC employing a silica gel phase impregnated with L-aspartic acid as chiral selector [3]. In this case, the racemic mixture was separated into its enantiomers although analysis times of 3.5 h were needed.

In this work, a screening of anionic cyclodextrins (CDs) was carried out in Electrokinetic Chromatography in order to select those with the highest potential to discriminate colchicine enantiomers. Using succinyl- and sulfated-γ-CDs, two chiral methodologies were developed to achieve the quality control of colchicine. A reversal in the enantiomer migration order for colchicine was observed with these cyclodextrins. Optimization of the experimental conditions for both cyclodextrins enabled to obtain enantiomeric resolutions of 5.6 in 12 min for succinyl-γ-CD and 3.2 in 8 min for sulfated-γ-CD. The analytical characteristics of the developed methods were evaluated in terms of linearity, accuracy, precision, and limits of detection (LOD) and quantitation (LOQ) and they were applied to the analysis of pharmaceutical formulations. The content of R-colchicine in these samples was below the LOD and the amount of S-colchicine was in good agreement with the labeled content.

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P-CPA-11

HIGH RESOLUTION MASS SPECTROMETRY FOR THE IDENTIFICATION OF *IN-VIVO* 5-MeO-MiPT METABOLITES IN MOUSE SERUM AND URINE

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The consumption of new psychoactive substances (NPS) has increased in the last years. New compounds are being continuously detected and identified in seizures and products sold on the Internet. There is therefore an increasing need of procedures to evaluate not only the identity of the NPS present in the legal highs but also their consumption. These procedures are commonly based on the detection of markers related with a specific compound, usually its metabolites, in biological fluids. High resolution mass spectrometry (HRMS) has proved to be a powerful technique for metabolite structure elucidation. This technique in combination with metabolism studies, such as *in-vivo* experiments, would allow obtaining consumption biomarkers for investigating drug use or intoxications.

In this work, metabolism of the tryptamine 5-MeO-MiPT was studied using liquid chromatography coupled to quadrupole-time of flight mass spectrometry (LC-QTOF MS) using adult male mice of the inbred strain C57BLJ/6. This allowed obtaining Phase I and Phase II metabolites in different biological fluids, such as urine and serum, and evaluating the metabolism of this compound over time. Thus, 16 µg of 5-MeO-MiPT (being in the range of a typical dose of 0.27 mg/kg) were injected i.p. to the mouse specimens, using NaCl 0.9% and 1% DMSO solution as drug carrier. Four groups of three specimens each were injected with the drug solution (150 µL), while one additional group of four specimens was injected with the drug carrier solution and used as control group.

Urine samples were collected at 60 min for one of the groups injected with the drug and for the control group. Urine samples were directly injected into the LC-QTOF MS system after simple dilution and also after hydrolysis with β-glucuronidase. Regarding serum samples, they were collected at 10, 20, 40 and 60 min for the drug groups, and at 60 min for the control group. Serum samples were injected after protein precipitation with acetonitrile, evaporation of organic solvent and reconstitution with the mobile phase.

The resulting metabolites were detected and tentatively identified making use of the accurate-mass information provided by QTOF MS for both (de)protonated molecule and fragment ions, after comparing control and positive samples. Additionally, the common fragment pathway and mass defect filter strategies were also evaluated.

P-NP-1

DIRECT DETECTION OF THE MONOTERPENE CARVACROL IN MAMMAL TISSUES BY ANALYTICAL PYROLYSIS (Py-GC/MS)

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Responding to consumer demands on minimal processing and preservative-free products, the use of essential oils (EOs) to extend shelf life of foods is on the spot in the food industry [1]. Carvacrol, main compound of Oregano EO, is registered as a flavouring in Europe; however, its use for other applications, such as active food packaging, may require higher concentrations and there is an increasing concern regarding exposure. Because of this, the European Food Safety Authority (EFSA) requires additional genotoxic studies data of substances which could be incorporated into food packaging like carvacrol. Here a detailed analytical pyrolysis (Py-GC/MS) study is conducted as a complement to *in vivo* genotoxicity studies.

Analytical pyrolysis was the technique chosen to search for carvacrol directly in viscera and to confirm that the compound effectively reached target tissues from orally exposed (0, 81, 256 or 810 mg carvacrol/kg bw, calculated according to carvacrol Maximum Tolerated Dose (MTD)) young adult male Wistar rats strain RjHan:WI*. Doses were prepared in corn oil at a final volume of 1 mL and during the treatment period, clinical signs, body weight, and food and water consumption were recorded daily. Rat stomach and liver composite samples were selected for pyrolysis and preserved at -80ºC until lyophilisation (Testal Cryodos, Madrid). Direct pyrolysis was performed in a double-shot pyrolyzer (Frontier Lab 2020i) attached to a GC/MS system (Agilent 6890N + 5973MSD). Detailed chromatographic conditions can be found in [2]. In short, lyophilized tissue (stomach and liver) were thoroughly homogenized and samples introduced (0.5 mg) into a preheated micro-furnace at 500 ºC for 1 min and evolved gases transferred to the GC/MS for analysis. Compounds assignment was via single-ion monitoring and by comparison with published and stored (NIST and Wiley libraries) data.

In a previous study, it was determined that pyrolysis of carvacrol does not to produce major effects on its chemical structure and therefore was considered an adequate technique to detect the presence of the monoterpene in animal tissues. The analytical pyrolysis of target tissues of control rats was negative to any sign of carvacrol even when searching for the specific mass fragments (m/z 135 and 150). However, carvacrol was clearly detected in the tissues of rats treated at all doses. Furthermore, when normalizing the chromatograms to a common peak, a clear dose response was obtained. A conspicuous difference was found in the dose-response curves between stomach and liver; whereas a direct lineal correlation could be drawn from the former, the response for the latter was best fit to a quadratic equation model. In this regard, the differences observed in those curves may be related to carvacrol metabolism in rats and the possible occurrence of saturation mechanisms limiting an excess of carvacrol metabolization/presence in liver.

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(*) The Ethics Committee on Animal Experimentation of the University of Sevilla approved the in vivo experiments. Moreover, in compliance with the Directive 2010/63/EU for the protection of animals used for scientific purposes all animals received humane care.

P-NP-2

CHROMATOGRAPHIC PROFILING OF *Camellia Spp.* SEEDS COMPOSITION

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Camellia is a plant belonging to family of Theaceae that is excellently adapted to the climate and soil of Northwestern Iberian Peninsula. In Europe, *Camellia* is usually grown as an ornamental plant, although it can also be evaluated as a source of bioactive compounds with demonstrated health properties, mainly omega-3 fatty acids (FA) and polyphenols.
In this work we present the results of the profiling of MSPD Camellia seeds extracts using both LC and GC with mass detectors. Compared to the so-called conventional techniques of extraction, the use of MSPD allows reducing the use of high organic solvent volumes as well as the simultaneous cleaning of the extracts, which lead to richer and cleaner extracts for the chromatography. Using an experimental design approach, factors influencing the efficiency of the MSPD have been evaluated. Among others, both the dispersant and solvent have been optimised, including in the study some uncommonly used solvents considered as green and then, with higher practical interest in the extraction of those bioactive components of the seeds. For the GC-MS analysis of FA, FAMES derivatives were obtained [1]. Different *Camellia* species were considered: *japonica, sasanqua, sinensis and reticulata* ("bigseed"). The FA profile showed that all varieties presented qualitatively similar composition, with the presence of oleic, linoleic, palmitic and stearic acids, whereas important differences were noticed in the quantitative content of the acids. The oleic acid content was about 80 % in all varieties with the exception of *C. sinensis*. The individual polyphenolic profile of Camellia spp. has been studied applying the previous experience of our group in profiling grapes and grape seeds [2,3]. These significant differences found in the composition of the studied varieties of Camellia spp constitute a potential for differentiated practical applications of the Camellia spp extracts [4].

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P-NP-3

PRESSURIZED LIQUID EXTRACTS OF *Cytisus scoparius* SELECTIVELY-ENRICHED IN POLYPHENOLS

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The extraction of plant phenolics from wild shrubs belonging to *Cytisus scoparius,* a greatly expanded leguminous, has been assessed. These brooms mainly grow in disturbed areas and their presence often favors the rapid spread of fire. But it has also been used in traditional medicine due to its diuretic, antidiabetic, hepatoprotective and sedative properties; recent publications also show its antioxidant activity probably related to its phenolic content [1]. The growing interest in this broom is joined to the fact that nowadays vegetable wastes and unexploited wild plants have become a remarkable source of bioactive compounds, so making necessary the characterization of these new potential raw materials.

Pressurized Liquid Extraction (PLE) was the technique chosen to characterize *Cytisus scoparius* from Galicia (NW Spain) [2]. The extraction solvent (nature and composition) was optimized by means of chemometric tools (Mixture Design, Simplex Centroid). Different parts of the plant have been separately considered. Thus, extracts of flowers, seed pods, seeds, and the entire plant, have been obtained and analyzed in order to get the phenolic total content, the antioxidant activity and the concentration of the major polyphenols. Folin-Ciocalteu method has been applied to get the total polyphenolic content while the antiradical activity has been measured by the free radical DPPH method. In order to get the concentration of the main polyphenolic compounds, samples have also been analyzed by HPLC-DAD and LC-MS-MS.

The results show important contents in phenols and remarkable antioxidant activity of the extracts, making the plant suitable as raw material to get bioactive compounds. Although all the polyphenols identified are associated with health benefits, some of the compounds are of particular interest. The best results have been found working with the whole plant extracts at high temperatures; although the selective processing (whole plants or parts) opens up new possibilities for obtaining differentiated extracts that are rich in certain polyphenols in particular or the full range of polyphenols associated with this plant species.

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P-OT-1

UHPLC-QTOF MS METABOLOMICS FOR BIOMARKER DISCOVERY IN NEURODEGENERATIVE DISEASES: ALZHEIMER AND CADASIL

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Untargeted metabolomics has become a powerful tool in several fields as the discovering of new diagnostic markers for diseases or highlighting metabolic alterations in patients. The huge number of compounds observed by high resolution mass spectrometry (HRMS) have become this technique in the most employed in this field, providing a sensitive and universal system for metabolomic studies. The good elucidation power of HRMS instruments in combination with mass spectral databases have lead us to select UHPLC-QTOFMS for this project. E280A is a specific mutation related to early appearance of Alzheimer Disease (AD), prevalent in small communities in Colombian areas [1]. Cerebral Autosomal dominant arteriopathy with subcortical infarcts leukoencephalopathy (CADASIL) is a strange and hereditary disease affecting the central nervous system with genetic diagnosis [2] being Neuroscience group from Antioquia University, one of the main experts in this disease.

In the present work, 19 plasma samples of each group (E280A, CADASIL, E280A control and CADASIL control) were included in this preliminary study. Samples were 10-fold diluted with acetonitrile and centrifuged for protein precipitation. 500 µL of supernatant were reserved for hydrophilic interaction chromatography (HILIC) analysis and the remaining, dried and reconstituted in H_2O:MeOH (90:10) for reversed phase (RP) chromatography. Afterwards, sample extracts were injected by liquid chromatography coupled to hybrid quadrupole time-of-flight mass spectrometry (UHPLC-ESI-QTOF MS) in both positive and negative ionization modes. Analysis were both carried out under HILIC and RP separations in order to maximize compound coverage.

Peak picking was performed by XCMS (R free package), retention time was aligned for all the samples, intensity was normalized with mean centering and log2 transformation was applied. Finally, pareto scaling was applied to maintain covariance between samples. Then, Orthogonal Partial Least Square – Discriminant Analysis (OPLS-DA) was used to highlight the most significant biomarkers. MS/MS experiments have been carried out for the elucidation of the selected biomarkers and, finally, their relevance in feasible biological processes related to these diseases have been studied. Some of these chemicals could become an important tool to diagnose or understand the processes affected by these disorders.

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P-OT-2

ORGANOLEPTIC CHARACTERIZATION OF VIRGIN OLIVE OIL BY HS-GC-MS

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In this communication we present the development of qualitative and quantitative, rapid and highly sensitive methodology for the analysis of volatile and semi-volatile organic components present in virgin olive oils for the organoleptic assessment thereof, as a complementary method to the official method (named panel test method).

The analysis is performed on a HeadSpace- Gas Chromathography- Mass Spectrometry (HS-GC-MS), working with electron impact ionization and SIFI mode for ion detecting (FULLSCAN and SIM at the same time, in a scan range of m/z 35-350 0.5 s/scan). Chromatographic separation is carried out on a 5% phenylsilicone GC column (60 m length, 0.32mm i.d. and 1 um film thickness). Extraction of volatile and semi-volatile components from olive oils, is conducted by the technique of static headspace from 2 g of sample, at 120 ° C for 15 min and with sample vial shaking in order to facilitate the analytes extraction. 1-Fluorobenzene is added to all samples as internal standard and used for the relative quantification of analytes (chemical markers). Under these conditions, we selected 39 compounds as marked compounds.

They were optimized chromatographic conditions, temperature of the transfer line HS/CG (200 ° C), mode injection headspace (balance of pressure to 30 psi for 0.15 min) and a direct injection on column avoiding losses of analytes minority.

With the experimental results obtained from the analysis of 550 olive oils previously characterized by accredited tasting panels we development different prediction models of the three olive oils categories, Extra-Virgin-Lampante by discriminant analysis and partial least squares regression (PLS-DA) gave optimal prediction results (>85%).

The method developed for the qualitative and quantitative characterization of volatile components, as well as the identification of chemicals with positive/negative attributes in samples of virgin olive oil with different organoleptic qualities.

P-OT-3

METABOLOMIC ANALYSIS OF SCROBICULARIA PLANA BY ORGANIC MASS SPECTROMETRY TO EVALUATE THE ENVIRONMENTAL STRESS

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Bioindicators can reflect the effects of pollutants on their metabolism, being widely used to assess environmental stress [1]. For this reason, the bivalve *Scrobicularia plana* has been proposed to monitor the contamination in final part of the Guadalquivir River estuary. For this purpose, the metabolic response of digestive glands, considered as the most metabolically active organ, of the clam *Scrobicularia plana* has been compared between an area of high pollution (Brazo de la Torre, BLT), which receives contaminants from the mining activity in the Iberian pyritic belt, with another area of lower pollution (La Pantoca, PAN), that was used as a control group.

Metabolomics is relatively new in the *omics* revolution, but has shown enormous potential for investigating biological systems and their perturbations. In this sense, it has been applied a metabolomic "workflow" to the clam *Scrobicularia plana* based on the complementary use of both techniques organic mass spectrometry by direct infusion mass spectrometry (DI-ESI-QqQ-TOF MS) and gas chromatography mass spectrometry (GC-MS)[2].

The results were statistically treated by multivariate partial least squares analysis (PLS-DA) and show a good classification between the studied groups. Only metabolites with VIP > 1.5 (Variable Influence on the projection) have been considered good biomarkers of environmental stress.

The integration of these two techniques provides several altered metabolites of biochemical pathways including energy metabolism, degradation of membrane phospholipids, β-oxidation and oxidative stress. These results confirm the possibilities of the applied metabolomics approach to get deeper insight into the metabolic response of living organisms to pollution

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P-OT-4

STUDY OF METALS INTERACTIONS AND METABOLIC CHANGES CAUSED BY CADMIUM EXPOSURE OF MOUSE *MUS MUSCULUS*. PROTECTIVE EFFECT OF SELENIUM.

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Cadmium is a widespread, highly toxic, environmental pollutant derived from natural and industrial sources, which is known to be accumulated in the human body. Once incorporated to organism cadmium readily gets liver, kidneys, and gastrointestinal tract, producing serious harmful effects that cause poor bone mineralization, anemia, retarded growth, developmental abnormalities and carcinogenic effects in humans[1–3] and experimental animals, such as mice. Moreover, Cd has long half-life in the body, and recently, Cd exposure has been associated with several endocrine effects[5]. On the other hand, it is well known that selenium presents numerous antagonistic interactions with Cd, such as prevention of oxidative stress induced by this element, protection against Cd-induced nephrotoxicity and hepatotoxicity, and antagonistic action against Cd-induced inhibition of hepatic drug metabolism.

For this reason, the use of analytical methods for obtaining massive information, such as metabolomic approaches, is of great interest to evaluate the effects of controlled exposure of *Mus musculus* to Cd and Se.

In this research, 40 specimens of *Mus musculus* were exposed during 15 days to oral (Se) or subcutaneous (Cd) administration of different doses of Se/Cd in mg per kg of body per day (mg kg^{-1} d^{-1}), that configures the following groups: GROUP A, 0.15 (mg kg^{-1} d^{-1}) of Se; GROUP B, 0.5 (mg kg^{-1} d^{-1}); GROUP C and D exposed to 0.15 mg and 0.5 mg Se respectively and both 0.1 mg Cd per Kg of body.

Metals (Cd, Se, Zn, Mn, Co, Fe, As, Pb, Cu) were measured by ICP-MS in different organs of exposed *Mus musculus* (liver, kidney, brain, lung and testis) and serum to study metals homeostasis and interactions. In addition, a metabolomics approach based on GC-MS was applied to establish alteration in metabolic pathways and defense mechanism triggered by Cd/Se exposure.

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P-OT-5

TARGETED METABOLIC PROFILING OF PHENOLIC COMPOUNDS IN STRAWBERRIES UNDER DIFFERENT POST-HARVEST CONTROLLED ATMOSPHERE TREATMENTS

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Strawberry (*Fragaria x ananassa*) fruit is a rich source of polyphenolics that has been claimed to have beneficial effects on human health related to their antioxidant activity, inhibition of low-density lipoproteins, decrease of cardiovascular diseases and some types of cancer [1]. The major challenge of post-harvest technology is to gets the consumer with a similar quality that harvested one and, if possible, with improved organoleptic properties. Strawberry post-harvest techniques often focus on the use of controlled atmospheres (CA), such as storage with low O_2 and high CO_2 concentrations and modified atmosphere packing (MAP) [2]. Until now, the effects of CA on the strawberry fruit have been confirmed in their quality attributes and chemical composition evaluated. The main changes in strawberry under enriched CO_2 atmosphere (10-40% of CO_2) occur in fermentation of metabolites in strawberry (acetaldehyde, ethyl acetate and ethanol), the concentrations of major organic acids (citric acid and malic acid) and phenolic content, which are closely related to ripe fruit [3]. In order to investigate strawberry fruit changes on the phenolic composition a targeted metabolic profiling analysis was conducted from ten fruit samples from each different controlled atmosphere treatments by ultra-high-performance liquid chromatography coupled to mass spectrometry (UPLC-MS). Freshly harvested strawberries were treated under different atmospheres with 10%, 20% and 30% of CO_2, containing always a 5% O_2 at 0ºC for 2 days. After 2 days of storage the samples were cryohomogenized and immediately frozen in liquid nitrogen and kept at -80ºC until sample preparation. The phenolic compounds of the fruit were extracted with a pre-cooled methanol/formic acid solution (3% of formic acid). The extracts were centrifuged at 10000 rpm for 5 min and filtered thought 0.45 µm [4]. Separation and identification of phenolic compounds were performed using an Accela UPLC chromatograph (Thermo Scientific) coupled to a UV-Vis diode-array detector and a QSART XL (Applied Biosystems) mass spectrometer equipped triple quadrupole (QqQ) coupled to a time of flight (TOF) analyzer with electrospray ionization. The phenolic profiles obtained were statistically compared using partial least squares discriminant analysis (PLS-DA).

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P-OT-6

COMBINATION OF GAS CHROMATOGRAPHY-MASS SPECTROMETRY FOR METABOLOMIC STUDIES OF INFLAMMATORY DISEASES

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Inflammatory processes are basic mechanisms of defense against organism's pathological episodes, consisting of a local reaction of the injured tissue. There are many environmental agents that can cause a chemical inflammatory response, including microorganisms, physical agents, and trauma.

Among the inflammatory processes one of the most important for its incidence is the psoriasis, a chronic inflammatory skin disease of autoimmune origin, which produces lesions with extensive clinical and evolutionary variability. Not much is known about the etiology of this disease, therefore the omics, and particularly metabolomics [2], can be a good tool to deep insight into the knowledge of this disease.

In this study, 39 female Swiss mice were exposed to 12-O-tetradecanoilforbol-13-acetato (TPA), in the dorsal area, to induce an inflammatory process similar to psoriasis disease. Previously, the animals were treated with tow algae extracts (MD and A-11) and a conventional drug for inflammation (dexamethasone- DEX). Serum, kidney and liver of the specimen were dissected and treated for metabolomic analysis by GC-MS.

For the extraction of serum metabolites from serum, 100 µL of this fluid was mixed with 400 µL of 1:1 methanol/ethanol mixture, centrifuged and dried under N_2 stream. For this study, metabolites are derivatized in order to increase the volatility of the analytes, stabilize the thermally labile analytes and improve their volatility for the chromatographic process. For this purpose, sample residues were treated with ~~of~~ 50 µL of methoxylamine hydrochloride (20 mg/mL in pyridine) at 70ºC for 40 min, followed by 50 µL MSTFA at 50ºC for 40 min. Analysis of kidney and liver samples was performed in a similar way, although metabolite extraction requires the use of 30 mg of tissue that was treated with 300 µL of methanol. Analysis by GC-MS was performed as published elsewhere [1], and identification of endogenous metabolites was based on retention time matching with standards or NIST Mass Spectral Library.

Finally, a pre-processing data including alignment of the peaks, normalization and noise suppression signal were performed, followed by partial least squares discriminant analysis (PLS-DA) to identify potential metabolic changes caused by inflammatory disease.

Multivariate analysis of the results shows a clear classification among different groups of mice. About 30 altered metabolites were found with significant differences among groups. The metabolomic response of the patient group is clearly different from the control group, which reinforces the hypothesis of the existence of metabolic systemic changes caused by psoriatic disease.

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P-OT-7

INVESTIGATION OF LUNG CANCER BIOMARKERS IN HUMAN BIOLOGICAL FLUIDS BY METABOLOMICS BASED ON GAS CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY

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Lung cancer (LC) is one of the most common causes of death by neoplasia in the world causing more than 1.3 million deaths per year [1,2]. The search of biomarkers in biological fluids for early diagnosis is currently a major challenge in medicine. In this regard, the use of metabolomics as analysis technique plays a key role, since it allows analyzing a large number of metabolites that may modify their concentration in response to metabolic disorders caused by the disease, and therefore, they could serve as diagnostic markers. In this study, we have developed a metabolomic procedure based on gas chromatography coupled to a mass spectrometer (GC-MS) to determine the metabolomic profiles in three biological fluids from patients with lung cancer: serum (S), urine (U) and bronchoalveolar lavage fluid (BALF). BALF is an interest fluid for LC diagnosis and provides information on actual pulmonary secretions. Our study provides new contributions to the pathology of the LC because there are no antecedents on the use of BALF for this purpose.

Pretreatment of S, U and BALF samples were based on the addition of alcoholic solvents and dryness using a speed vacuum system. In the case of urine, urease was used to remove the urea interference in mass spectra. Finally, a derivatization step was necessary before the injection into GC-MS. A total of 90 serum, 90 urine and 55 BALF samples from patients with LC, patients with lung diseases without cancer, LD, and healthy patients, C, were analyzed in order to compare the metabolomic profiles of these three types of samples, in order to establish metabolic differences between them. Multivariate analysis, PLS-DA, presented a clear classification of study groups for all types of samples, indicating the existence of altered metabolites in LC. Twenty two, eighteen and twenty perturbed metabolites in LC were identified in S, U and BALF, respectively, involved in different metabolic pathways associated with the cancer pathology. Furthermore, the study of metabolic pathways indicated that the metabolism of glycine, threonine and serine was the most disturbed in LC. Finally, to evaluate the specificity and sensitivity of metabolites altered, ROC (receiver operator characteristic) curves were applied to the dataset and metabolites with “area under the curve” (AUC) higher than 0.75 were considered as potential biomarker of LC.

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P-OT-8

IN-SOURCE FRAGMENTATION FOR METABOLITE IDENTIFICATION IN CE-TOF-MS APPLIED TO THE CHARACTERIZATION OF PLASMA SAMPLES

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Capillary electrophoresis/electrospray ionization mass spectrometry (CE-ESI-TOF) has been widely used in the metabolomic study of plasma samples. With this technique various types of analytes have been determined, mainly polar and ionic compounds, providing an analytical tool orthogonal to LC-MS. Although there have been many metabolomic studies in different types of samples achieving some very important results, there are always some unidentified compounds. Among different methods for metabolite identification or ID confirmation, tandem MS analysis plays a very important role. However, not all analysers are suitable for tandem MS measurement e.g. TOF-MS. In addition to this, the lack of commercially available standards makes identification a difficult task. For this purpose our group proposed a novel use of induced in-source fragmentation, by enhancement of the fragmentor voltage, with the aim of obtaining information about the fragmentation pattern of metabolites [1].

This method has been tested in a plasma pool, in a standard reference material human plasma (SRM 1950) and solutions containing mixtures of standards, with the aim of deciphering the total metabolome obtained with CE-MS. Separations were carried out in normal polarity in a fused-silica capillary (100 cm x 50 µm i.d.) with a background electrolyte containing 1 M formic acid in 10% methanol (v/v) at 20°C. Separation conditions were 25 mbar pressure and 30 kV voltage. The sheath liquid used consisted of 50 % methanol, 50 % water, 4 µL formic acid, and two reference masses: 121.0509 and 922.0098. The MS parameters were: fragmentor 100 V or 200 V, Skimmer 65 V, octopole 750 V, nebulizer pressure 20 psi, drying gas temperature at 200ºC and flow rate 10.0 L/min. The capillary voltage was 3500 V. Data were acquired in positive mode with a full scan from *m/z* 50 to 1000.

Only, ions present across all replicates from the plasma pool (n=6) in at least one of the two groups analyzed (fragmentor voltage 100 V or 200 V) were kept for further identification. CE-MS analysis of plasma detected 132 features in 200V and 98 features in 100V, 57 were identified based on database, isotopic pattern and possible presence in biological fluids. Besides, the proposed methodology was successfully used for quick differentiation between two metabolites with the same monoisotopic mass.

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P-OT-9

PREDICTION OF HUMAN METABOLIC CLEARANCE OF ROSEMARY DITERPENES BY UHPLC-TOF MS ANALYSIS OF METABOLITES IN HEPARG CELL CULTURE SAMPLES

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The oral bioavailability and metabolism of dietary phenolics has become major concerns in phenolic chemopreventive and cancer therapy research. Similar to other xenobiotics, phenolic compounds are regarded by the body as foreign compounds. As a result, after ingestion and absorption, they are highly metabolized, resulting in metabolic forms (that may possess biological properties markedly different from those present in foods) being present in the body. In recent years, the inhibitory effect of rosemary diterpenes on proliferation of colon cancer cells has been investigated at the transcriptomic, proteomic and metabolomic [1-3]. In the present work, the metabolic clearance of the rosemary diterpenes carnosic acid (CA), carnosol (CS), and rosmanol (RS) were determined in differentiated HepaRG cell system, a cell model that retains most liver functions, including cytochrome P450-drug-metabolizing enzymes. The rates of hepatic metabolism of diterpene compounds were experimentally measured after the incubation of HepaRG cells with 25 µM of each diterpene for different time points (up to180 min). Cell culture media and intracellular content of HepaRG cells were analyzed by ultra-high pressure liquid chromatography (UHPLC) coupled to time-of-flight (TOF) mass spectrometry (MS). By UHPLC-TOF MS, valuable information about the identity and formation rate of the metabolites derived from the hepatic cell transformation of CA, CS and RS, was obtained. The calculated parameters were scaled using *in vivo* scaling factors. These findings are very useful to gain additional insights on mechanistic information of the effect of rosemary polyphenols and their metabolization.

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P-OT-10

HIGH RESOLUTION MASS SPECTROMETRY IN THE IDENTIFICATION OF METABOLITES AND TRANSFORMATION PRODUCTS FROM ENROFLOXACIN IN THERMALLY TREATED MILK FROM MEDICATED COWS

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The presence of antibiotics and their metabolites, and/or products produced in subsequent treatments at which food is submitted before consumption, may be responsible for bacterial resistance, allergy and/or toxicity on sensitive individuals [1]. Therefore their study constitutes a challenge considering food safety issues [2,3].

In this context, Enrofloxacin (ENR) is a fluoroquinolone used in veterinary to treat infectious illnesses such as mastitis in cows. In the work here presented we have studied the presence of metabolites from ENR in milk samples. We have also considered their evolution following thermal treatment. This procedure permits to simulate pasteurization and/or sterilization which milk is submitted before commercialization.

Milk samples from cows medicated with ENR were collected during the three days of pharmacological treatment and for four days after finishing it. All samples were heated at 120^{o}C during 20 and 60 min (T120.20 and T120.60) to simulate the effect of temperature applied to milk before consumption.

The resulting heated and non-heated samples were analysed by liquid chromatography coupled to high resolution mass spectrometry (LC-HRMS). Data were acquired in full scan mode to get information about all compounds in the 150-450 Da range. MZmine software was used to obtain a list of *m/z* values corresponding to compounds whose concentrations underwent modification either during the pharmacological process or because of the thermal treatment.

Principal Component Analysis (PCA) was applied to the obtained results in the search of compounds allowing us to classify samples according to the stage of the pharmacological treatment and to discern heated samples from those non-heated. The structures of some of the detected compounds of interest were elucidated thanks to their high resolution MS^2 spectra.

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P-OT-11

STUDY OF THE POLAR METABOLOME BY REVERSED-PHASE LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY. EVALUATION OF DIFFERENT SAMPLE PREPARATION METHODS FOR PLASMA PROFILING

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Metabolic profiles provide useful information related to the state of an organism as they are directly related to the cellular activity and are correlated with phenotype in a more direct manner than the rest of the '*omics*' [1]. Amino acids and their metabolites are molecules which play important roles in numerous metabolic pathways, serve as building blocks for proteins, and act as biomarkers of several disorders [2]. However, most of these compounds are unable to be retained on Liquid Reversed-Phase Liquid Chromatography (RPLC) due to their high hydrophilic character. An interesting and easy strategy is to reduce their polarity through their derivatization with a labelling reagent, such as the commercially available 9-fluorenylmethyloxycarbonyl (FMOC) which offers many advantages such as forming stable complexes with primary and secondary amine moieties rapidly, improves the chromatographic separation, and also enhances the selectivity and sensitivity. Although some derivatization reagents have been employed in the study of metabolic profiles, FMOC has never been employed for this purpose.

Herein, the use of FMOC as labelling agent is shown to offer better performance in the determination of a group of 35 polar compounds (amino acids and amines) in a C18 column, when compared to other polar stationary phases without using compound-labelling, not only in the number of retained compounds but also in terms of sensitivity and peak efficiency. Different strategies for protein elimination were also carefully evaluated in plasma and results revealed that ultrafiltration gave rise to a larger number of compounds with a lower variability from sample to sample when compared with the protein precipitation method. Finally, the suitability of the proposed methodology in the metabolic profiling of plasma samples is also demonstrated.

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P-OT-12

A CROSS-PLATFORM METABOLIC WORKFLOW FOR VOLUME-LIMITED TISSUE SAMPLES. APPLICATION TO THE MICE MODEL OF POLYCYSTIC KIDNEY DISEASE

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Metabolic profiling provides an unbiased view of the physiological status of an organism as a "function" of the metabolic composition of a measured sample. The diversity of physicochemical properties of the metabolites forces implementation of cross-platform strategies for improving the metabolite coverage. This, however, may become a challenging task when volume-limited samples are to be analyzed.

One of the examples of volume-restricted samples are histological tissues section, which not only are limited with regard to the material abundance, but also require tailored extraction procedures. Here, we propose a simple Liquid Chromatography-Mass Spectrometry (LC-MS) based workflow for metabolic profiling of histological 20 µm-thickness sections of mouse kidney. We aimed our efforts on re-using the material so that once samples were analyzed in LC in the reversed-phase mode, the remaining sample was analyzed in the hydrophilic interaction liquid chromatography (HILIC) mode, after a phase changing step. It is confirmed that no significant difference in the number of obtained features was observed between a sequential analysis and the direct analysis in the HILIC system.

Finally, in order to demonstrate whether the proposed metabolic workflow was able to provide relevant information describing a biological experiment, we selected kidney section samples from an experimental model of polycystic kidney disease (PKD). Our metabolic workflow enabled to observe differences in the progression of PKD and a subset of metabolites which were differentiating the studied groups could be identified. This demonstrates the applicability of the proposed metabolic workflow where valuable biological information was obtained although the amount of biological material employed was extremely limited.

P-OT-13

STUDY OF SEVERITY IN FOOD ALLERGY LINKED TO RESPIRATORY ALLERGY THROUGH METABOLOMICS

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Allergies are increasing steadily worldwide, the current prevalence in the western world is estimated for about 25% of total population. Moreover, in recent decades there have been both, a progression and greater severity of various diseases, such as asthma, food allergy or medication allergy. In the case of food allergy, several studies using the allergen profiling have been published. Profilin has proved that allergens may have effective access through the path of the oral mucosa, creating a new paradigm in the study of food allergy and became a unique model to study the evolution of allergic inflammation. Moreover, Spain is an ideal place to study the correlation between exposure and development of food allergy due to its extreme climatic variation [1]. To date, there is a huge lack of deep knowledge concerning the molecular metabolism involved in this pathology. Therefore, metabolomics emerged as a capable science used to manage complex multifactorial diseases thought the analysis of all possible metabolites in a biological sample obtaining a global interpretation of biological systems. Here, one of the most used techniques is liquid chromatography coupled to mass spectrometry (LC-MS), which attempts to detect the majority of the compounds extracted from liquid or solid samples. In this study, we propose to perform the metabolic profiling characterization of allergic patients and controls, in order to look for biomarkers that might predict the prognosis of the disease and to understand the molecular mechanisms of inflammation underneath the disease. Plasma samples from 4 groups; controls, mild, moderate and severe allergic patients to profilin were measured by LC-MS in both polarities. The samples were from 3 hospitals in Madrid and one in Plasencia in Spain. The data obtained was analysed using multivariate and univariate statistical tools. The results from the statistical models showed differences between the groups. Significant masses of each comparison were tentatively identified using several web databases. From the tentative compounds, metabolites from energy metabolism, aminoacids, fatty acids, sphingolipids, phospholipids and bile acids were found significant correlated to the severity of the disease. Moreover, in our study significant differences were also found between the locations of patients, which matched as Plasencia is known to show extreme allergic phenotypes due to the high exposition.

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P-ENV-1

DEVELOPMENT OF A DISPERSIVE LIQUID-LIQUID MICROEXTRACTION GC-MS/MS METHOD FOR THE DETERMINATION OF WATER FRAMEWORK DIRECTIVE PRIORITY POLLUTANTS IN WATER SAMPLES

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In the field of water policy, the European Union (EU) adopted the Directive 2013/39/UE [1] amending the Water Framework Directive (WFD) 2000/60/EC [2] and Directive 2008/105/EC [3]. Moreover, environmental quality standards were established in Directive 2008/105/EC in order to define the maximal concentrations of priority pollutants authorized in different types of waters. More recently, the Decision 2015/495 [4] of the EU has published a watching list with some new priority pollutants that must be monitored and considered in the future revisions. So, there is a need to develop simple and fast methods able to analyze a high number of these substances at low detection limits to be used for routine laboratories.

Dispersive liquid-liquid microextraction (DLLME) is a technique that incorporates sampling, concentration and sample introduction into a single step. It offers high enrichment factors, uses low volumes and has several advantages, such as simplicity, rapidity, low cost and ease of method development. Its versatility and applicability to different problems and fields explain its development in the last years. As regards to environmental applications, it has been used for the analysis of several contaminants in water such as pesticides, PAHs, PCBs or PBDEs in water [5]. DLLME is based on the dispersion of tiny droplets of an organic extraction solvent into the aqueous phase which favors the kinetics of liquid-liquid extraction of analytes.

The present work describes the development of a multiresidue method, based on DLLME- gas chromatography coupled to tandem mass spectrometry (GC-MS/MS) for the determination of 32 WFD priority pollutants, including several pesticides, PAHs and BDEs in environmental waters. Factors relevant to the microextraction efficiency [6], such as the extraction solvent, the disperser solvent, their volume and the salt effect were optimized. Finally, 75 µL of 1,1,2-trichloroethane as extraction solvent, 3.2 mL of acetonitrile as disperser solvent and 4 g of sodium chloride were used.

The optimized method was validated in drinking water (DW), surface water (SW) and effluent wastewater (EWW) according to ISO 17025. Quality parameters including recoveries, linearity, precision and limits of quantification (LOQs) have been established for all the compounds. Recoveries higher than 85% were obtained and method LOQs lower than 9 ng/L were achieved for all analytes and matrices. Finally, to demonstrate the applicability of the method, samples from Llobregat River (Catalonia, NE Spain), effluent wastewater samples from two different wastewater treatment plants (WWTPs) and raw and treated water from Sant Joan Despí drinking water treatment plant (DWTP) were analyzed.

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P-ENV-2

ASSESSMENT OF TOTAL AND AVAILABLE POLYCYCLIC AROMATIC HYDROCARBONS IN BIOCHARS

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Biochar may act as a soil conditioner, enhancing plant growth by supplying and retaining nutrients and by providing other services such as improving soil physical and biological properties. Different feedstock, such as organic waste derived from agriculture and forestry or urban wastes including sewage sludge, can be used for biochar production. Feedstock properties and production conditions will drive the properties and composition of produced biochars [1]. Special attention should be paid to polycyclic aromatic hydrocarbons (PAHs), these persistent organic pollutants are highly condensed aromatic structures formed during biochar production due to incomplete combustion (pyrolysis step) [2]. These PAHs may enter the environment when the biochar is applied as soil conditioner, thus the intention of this study was to test a potential hazardous impact due to the presence of PAHs in biochars. Two different PAHs extraction techniques were applied to evaluate the total and available PAHs content in biochars. In order to find a relationship between pyrolysis conditions, feedstock and abundance of PAHs, four biochars produced from different feedstock were analyzed. Three biochars were produced by technical pyrolysis (500-600 ºC; 20 min) from wood, paper sludge and sewage sludge respectively (samples B1, B2 and B3). The fourth biochar was made from old grapevine wood provided by Bodegas Torres Company (Spain) and using the traditional carbonization method in kilns (kiln-stack wood biochar; B4). A detailed characterization of these samples can be found in [3].

Exhaustive extraction: The total concentrations of the 16 US EPA PAHs were determined by extracting the biochars during 12h under continuum reflux with 100% toluene. Analysis of PAHs was carried out on an Agilent GC/MS 6890/5973i by on-column injection of 1 µL of the extract. Chromatographic and mass spectrometric conditions applied are described in [1]. Non-Exhaustive extraction: Cyclodextrins (CDs) have been proposed as alternative agents to enhance the water solubility of hydrophobic compounds. CDs have a low-polarity cavity within which organic compounds of the appropriate shape and size can form inclusion complexes [4]. The selected CD was hydroxypropyl-β-CD (HPBCD), which has been widely used for this purpose in contaminated soils. ild extractions were performed using an 50 mM HPBCD solution as extractant containing 0.01 M $Ca(NO_3)_2$ as background electrolyte and 200 mg L^{-1} $HgCl_2$ to prevent bacterial growth. Biochar samples (2 g) were placed in glass tubes containing 20 mL of extractant, and the tubes were placed on an orbital shaker at 100 rpm during 24 hours.

Total PAHs yielded between 3167 (B3) and 6626 (B4) µg kg-1. The PAHs concentration of B4 was a 50% higher than B1. Taking into account that both biochars (B1 and B4) are produced from wood, it can be concluded that the pyrolysis process of B4, which was produced by carbonization in traditional kilns, affected significantly the total PAHs levels.

The non-exhaustive extraction procedure resulted in closer abundances of PAHs, which ranged from 978 (B3) to 1585 (B1) $\mu g kg^{-1}$. These data pointed that c. 15-35% of total PAHs present in biochars are extracted by CDs, and this amount could be considered as the fraction actually bioavailable. This parameter shoud be taken into account to determine the potential hazardous impact of the use of biochar as soil amendment.

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P-ENV-3

METHOD DEVELOPMENT FOR PERFLUORINATED (PFAC) AND PHTHALATE COMPOUNDS IN SEAWATER SAMPLES

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During the Barcelona World Race 2014th edition, Sailing Technologies in collaboration with the FNOB used a sampling device in the IMOKA ship developed by IQS. At the end of the race, this device provided a total of 90 seawater samples taken all around the world. Each sample is composed by some filters of different porous size and a solid phase extraction cartridge. A global study extracting as much information as possible from this set of samples has been started. The purpose of the present work is to study some of the organic contaminants retained by the SPE cartridges.

The families of compounds selected are PFAC (including carboxylic acids and sulfonates) and phthalates. With the purpose of obtaining a screening method for those families, an ultra-performance liquid chromatography method coupled to a tandem mass spectrometer detector has been developed.

Chromatographic conditions have been optimized using:

1) 7 different chromatographic columns
2) Formic acid or ammonium hydroxide as aqueous phase
3) Acetonitrile or methanol as the organic phase.

Regarding the detection method, SRM has been obtained for each compound optimizing every step of the detection process.

In order to prove the capabilities of this method, a 5 samples subset were analyzed to obtain the PFAC and phthalate content. Method allows the detection of fg/mL

High-Res QTOF system has also been used with these 5 samples. Based on the exact mass, main detected compounds have been identified with the purpose to use it in a principal component analysis (PCA).

P-ENV-4

LIQUID CHROMATOGRAPHY QUADRUPOLE TIME-OF-FLIGHT DETERMINATION OF SIX DRUGS IN VEGETAL BIOTA FROM DOÑANA´S NATIONAL PARK.

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To date, the concerns about accumulation and presence of emerging contaminants in plant matrices has focused mainly on assessing the presence and effects on food crops that may have consequences for human health through the food chain [1]. The purpose of the development of this analytical methodology is, to provide a tool for further application in the study on the risk of pharmaceutical substances to the environment, once released through wastewater discharges and direct incorporation into the vegetal biota and indirect animal biota, through that.

In the present work, we describe the development of a high sensitivity method of analysis using high performance liquid chromatography coupled to quadrupole time of flight detection (UHPLC-Q-TOF) to determine carbamazepine, ciprofloxacin, enrofloxacin, diclofenac, flumequine and ibuprofen in samples of *Lavandula dentata, European Salicornia* and *Juncus sp*.

Several columns with different characteristics were assayed for the chromatographic separation of the selected analytes: Zorbax Eclipse XDB C_{18}, 3.5 µm particle size x 4.6 x 150 mm; Acquity BEH C_{18}, 50 mm x 2,1 mm I.D., 1,7 µm particle size and Gemini C_{18} 5 µm particle size x 150 mm x 4.6 mm I.D. Best results for the posterior application to vegetal biota were obtained with Zorbax Eclipse XDB C_{18}, 3.5µm particle size x 4.6 x 150 mm.

Extraction of 0.5 g vegetal lyophilized sample was achieved with microwave energy at 50 W power for 5 minutes using a mixture acetonitrile: H_2O (50:50 v/v) as extractant solvent. Subsequently, the extracts were centrifuged for 20 minutes at 6000 rpm, the supernatant taken for further five-fold dilution with an acetonitrile:H_2O (50:50 v/v) solution. Diluted extracts were microfiltrated through 0,2 µm before LC-ESI-QTOF-MS injection.

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Acknowledgments: Ministerio de Economía y Competitividad. Proyect CTM2015-67902-C-1-P y Feder Funds project UNSE10-1E-429.

P-ENV-5

ASSESSING PALEOCLIMATIC CHANGES ARCHIVED IN SPELEOTHEMS FROM VOLCANIC CAVES BY PYROLYSIS GAS CHROMATOGRAPHY-BASED ANALYSES

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Speleothems, or secondary mineral deposits found in caves, are formed due to dissolution of primary minerals from the host rock and subsequent precipitation. Their formation is greatly prompted by water-rock interactions and climate conditions, which dictate how much water drip into the cave system [1]. In humid climates or during heavy precipitation a relatively rapid speleothem growth may occur, whereas in arid climates or during drought the growth is moderated or ceased. Hence, the composition, abundance and growth pattern of speleothems may be indicative of climate changes, as reported by several authors [1-2].

This study comprises a multidisciplinary approach based in the combination of chromatography (analytical pyrolysis and pyrolysis compound-specific isotope analysis) and stable isotope analysis for characterizing organic compounds entrapped in speleothems from volcanic caves. Samples collected in lava tubes were selected for this study: (i) coralloid speleothems from Easter Island (Chile), and (ii) moonmilk deposits from La Palma (Canary Islands, Spain). The aim was to recognize environmental changes during speleothem formation.

The coralloid speleothems from Easter Island consisted of three major layers with different mineralogical composition and a significant contribution of organic carbon. Analytical pyrolysis (Py-GC/MS) revealed contributions from higher plants and microorganisms to the organic matter entrapped in the coralloid speleothems. Biogeochemical analyses based on isotopic signatures and pyrolysis compound-specific isotope analysis (Py-CSIA) revealed that the genesis of the three colored layers was related to two different stages of speleothem formation caused by environmental changes on Easter Island. Variations in $\delta^{13}C$ values pointed to wetter conditions during the formation of the innermost layer and a water shortage during the latest stage of speleothem formation. The trend observed for $\delta^{15}N$ values suggested an increase in the average temperature over time, which is consistent with the so-called climate warming during the Holocene [3].

The chromatograms of the moonmilk deposits from Canary Islands evidenced the presence of organic compounds in their composition, in particular fatty acids, polysaccharides, phytosterols and oleanane-type triterpenes. Most of them have been previously found in sedimentary records. Oleananes and specific steranes are believed to derive from the early diagenesis of gymnosperms [4]. Our data suggest that the organic compounds associated with moonmilk deposits are partially driven by the topsoil and vegetation overlying the cave system. Hence, Py-GC/MS and Py-CSIA could be used as a valid proxy for paleoenvironmental research.

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P-ENV-6

ATMOSPHERIC PRESSURE CHEMICAL IONIZATION –GAS CHROMATOGRAPHY FOR THE CHARACTERIZATION OF CHLORINATED PARAFFINS

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Chlorinated paraffins (CPs), also referred as polychlorinated n-alkanes, are mixtures composed by thousands of isomers that represent a challenge for quantification in environmental samples. These compounds are currently analysed by gas-chromatography coupled to electron capture negative ionization-low resolution mass spectrometry (GC-ECNI-LRMS). However, mass interferences among different CP congener groups can occur due to the fragmentation obtained using ECNI. To overcome this problem high-resolution mass spectrometry (HRMS) is recommended. An additional disadvantage of GC-ECNI-LRMS methods is that the response is highly dependent on the chlorination degree of CPs [1]. This makes critical the selection of an adequate CP mixture as reference standard for quantitation and the use of quantitation procedures that minimize this dependence must be applied [2].

In the present work with the objective to overcome some of the limitations of the GC-MS methods, the potential of atmospheric pressure chemical ionization (APCI), a soft ionization source is evaluated. For this purpose, a new APCI source (commercially named APGC) was coupled to gas chromatography and used for the characterization of CP mixtures. This coupling has demonstrated to be useful for the analysis of non-polar halogenated compounds [3]. In order to improve ionization of CP congeners, chlorine enhanced negative ion APCI has been previously used coupled to liquid chromatography [4] or directly coupled to high-resolution mass spectrometry [5]. In the present work, an APCI source coupled to a quadrupole time of flight (QTOF) analyser was tested to assess the ionization and fragmentation behaviour of short-chain chlorinated paraffin mixtures (SCCPs, C_{10}-C_{13}) and individual CP congeners. The formation of the $[M+Cl]^-$ adduct ions was promoted by the addition of an halogenated reagent gas to the source. Several chlorinated organic solvents of high volatility were tested to enhance adduct formation avoiding in-source fragmentation and the best results were obtained using dichloromethane. Other APCI-QTOFMS parameters, such as source temperature and cone voltage, were also optimised. The developed GC-APCI-QTOF MS method was used for the characterization of SCCPs in technical mixtures and its applicability for quantitation of SCCPs in environmental samples was evaluated.

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P-ENV-7

SIMULTANEOUS DETERMINATION BY HPLC OF PYRETHRINS AND PYRETHROIDS IN WATER AND SEDIMENT SAMPLES

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Pyrethroid pesticides (PYRs) are a large group of synthetic analogs of the natural insecticide pyrethrum (a mixture of pyrethrin, cinerin and jasmolin) found in Chrysanthemum cinerariaefolium. These neurotoxins produce a rapid paralysis or quick knock-down effect on target pests. Pyrethroids are widely used indoors to control household pests, such as flies, mosquitoes, cockroaches, termites, and other harmful insects. The widespread use of these compounds has resulted in contamination of environmental compartments [1].

Due to their volatility, these substances are usually analyzed by GC-MS. In this work, as an alternative, a fast and sensitive multi-residue method that includes UHPLC-MS/MS determination for the target analysis of 11 pyrethroids and 6 pyrethrins is presented. Solid Phase Extraction (SPE) and a simple Dilute and Shoot method were developed for water and sediment, respectively. Acrinathrin, etofenprox, cyfluthrin, esfenvalerate, cyhalothrin, cypermethrin, flumethrin, bifenthrin, fluvalinate, deltamethrin and tefluthrin as pyrethroids as well as cinerin I, jasmolin I, pyrethrin I, cinerin II, jasmolin II and pyrethrin II as natural pyrethrins were the target compounds.[2]

The protonated molecule [M+H]+ and several adducts [M+Na]+ and [M+NH3]+ were tested as precursor ions. The most intense signal was for [M+NH3]+ for synthetic pyrethroids and [M+H]+ for the natural ones. The optimal fragmentor for product ions varied from 66 to 94 eV and the collision energy ranged between 5 to 82 eV. Recoveries ranged between 60 to 97 % and 79 to 108 % for water and sediment respectively. The LODs were < 10 ng/L in water and < 25 ng g-1 for sediments.

The analytical methodology proposed for the determination of pyrethrins and pyrethroids residues in environmental samples attains detection and quantification of residual levels of pyrethroids below of the maximum residue limits (LMRs) established by the European Union.

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P-ENV-8

ANALYTICAL CAPABILITIES OF GAS CHROMATOGRAPHY COUPLED TO HIGH RESOLUTION MASS SPECTROMETRY FOR THE ULTRA TRACE DETERMINATION OF CONTAMINANTS IN SURFACE WATER

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Organic pollutants are present in the enviroment mainly due to different anthropogenic activities such as agricultural or industrial chemical production. The combination of their extensive use and physicochemical and toxicological properties make it possible that these compounds end up in surface water, causing a potential risk for the enviroment and human health. With the aim of controlling and preventing contamination of aquatic ecosystems the European Union (EU) introduced the Water Framework Directive (WFD) which establishes guidelines to control the pollution of surface water indicating a list of priority substances and setting out environmental quality standards (EQS) for those chemicals [1].

The increasingly stringent regulations imposed by the EU and the United States Environmental Protection Agency (U.S. EPA) make it necessary to develop robust, reliable and highly sensitive and selective methods capable of simultaneously determining a broad range of organic pollutants at ultra-trace levels. In this regard, the application of high resolution mass spectrometry (HRMS) has been considered as a potential tool for the analysis of pollutants in environmental samples due to its high sensitivity and specificity. In order to do so, an automated method which enables the determination of 58 organic pollutants in surface water has been developed. The proposed method is based on an on-line combination of solid phase microextraction (SPME) and gas chromatography coupled to magnetic sector high resolution mass spectrometry (GC-HRMS) allowing for the determination of pesticides, polyaromatic hydrocarbons (PAHs), polychlorinated biphenyl congeners (PCBs) and polybrominathed diphenyl ethers (PBDEs), most of which are considered priority substances, others are currently under revision by the EU.

Firstly, SPME-GC-HRMS conditions were optimized so as to achieve optimal sensitivity and selectivity of the technique. Then, the developed methodology was fully validated showing good linearity, sensitivity and recoveries for most of the compounds included in the study and finally, it was successfully applied to the analysis of surface waters collected in Andalusia (South of Spain).

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P-ENV-9

REMOVAL OF ORGANIC MICROPOLLUTANTS IN WASTEWATER TREATMENT SCHEMES

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It is well known that organic micropollutants originated from urban and industrial activities are not completely eliminated during conventional wastewater treatment, which not only compromises the quality of receiving water bodies but also limits water reclamation and reuse, critical in the development of sustainable strategies for water resources management. The present study aims to evaluate the removal of organic micropollutants in a pilot treatment scheme involving a membrane bioreactor (MBR) followed by a hybrid powdered activated carbon nanofiltration (PAC-NF) operated in Baix Llobregat Water Reclamation Plant (Barcelona, Spain). The efficiency of the MBR pilots has been compared against the full-scale basic reclamation scheme of the plant, consisting of coagulation-flocculation followed by ballasted sedimentation, disk filtration and UV disinfection. On the other hand, the efficiency of the PAC-NF pilot has been compared against the full scale ultrafiltration (UF) and reverse osmosis (RO) advanced treatment of Baix Llobregat Water Reclamation Plant, the final effluent of which consists in a 50 % blend of both UF and RO.

Seventeen organic compounds (9 pharmaceuticals, 6 pesticides and 2 alkylphenols) were selected as target analytes in order to represent a wide range of micropollutants occurring in waste waters. A method based on solid phase extraction (SPE) coupled online with liquid chromatography and tandem mass spectrometry (LC-MS/MS) with electrospray ionization was developed to determine the presence of those compounds in waste and treated waters. Two different methods were required for positive and negatively ionisable compounds. The best chromatographic separation was obtained using a biphenyl reverse phase column with core shell particles and a gradient between water and methanol for the negative ionization method and acidified water and acetonitrile for positive ionization. Complete separations were achieved in 14 and 12 minutes chromatographic runs, respectively. OASIS HLB cartridges yielded the best recoveries for the SPE. Elution of the cartridges was carried out with 100% organic phase by means of the focusing mode, which avoided peak broadening caused by chromatographic separation in the cartridge when elution is accomplished with the LC mobile phase. These conditions allowed quantification limits between 5 ng/L (diclofenac and terbuthylazine) and 100 ng/L (acetaminophen) from 2 mL water samples. Furthermore, the use of the fully automated online technology enabled the reduction of total analysis time from almost a whole day to 26 minutes.

The results show the potential of hybrid PAC membrane processes to achieve high-level treatment of most organic micropollutants.

P-ENV-10

MULTI-RESIDUE ANALYSIS OF 36 PRIORITY AND EMERGING POLLUTANTS IN MARINE ECHINODERMS (HOLOTHURIA TUBULOSA) BY LIQUID EXTRACTION FOLLOWED BY DISPERSIVE SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY–TANDEM MASS SPECTROMETRY ANALYSIS

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Marine ecosystem tends to end up accumulating a huge variety of organic pollutants, primarily resulting from anthropogenic activities, through rivers, direct discharges, or atmospheric deposition. The use of marine echinoderms has been pointed as an integrative target sample because they are a common filter feeder widely distributed in sea coasts and thereby extensively exposed to xenobiotics from anthrophogenic sources [1,2]. In this context, a multi-residue method for the analysis of 36 organic compounds, among of most problematic emerging and priority pollutants, in *Hotothuria tubulosa* is validated and subsequently applied to determine the levels of target analytes in this organism presents along the coast of Granada (Spain), as well as in sediment samples.

Target compounds included perfluoroalkyl compounds, parabens, benzophenones, estrogens, plasticizers, surfactants, brominated flame retardants and alkylphenols. The procedure involves a simplified sample treatment including steps of liophilization, solvent extraction and dispersive clean-up of the extracts prior to liquid chromatography–tandem mass spectrometry analysis. The most influential parameters affecting the extraction and the clean-up step were optimized using design of experiments. In the validation stage, successful linearity (R^2> 0.990), recoveries (between 57 and 121 %), precision (RSD lower than 20 %) and limits of quantification between 0.025 and 12.5 ng g^{-1} d.w. levels were achieved.

The results highlighted a bioaccumulation of certain targeted pollutants in marine organisms, being quantified 25 out of 36 compounds in natural samples. Surfactants, alkylphenols, perfluoroalkyl compounds, triclocarban and parabens were the most frequently detected. The highest concentrations were measured for nonylphenol, reaching up to 340 and 323 ng g^{-1} d.w., in sediment and in holothuria samples, respectively.

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P-ENV-11

DETERMINATION OF SELECTED PARABENS, BENZOPHENONES, TRICLOSAN AND TRICLOCARBAN IN AGRICULTURAL SOILS AFTER AND BEFORE TREATMENT WITH COMPOST FROM SEWAGE SLUDGE. A LIXIVIATION STUDY

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The composting processes must be made adequately for an efficient and safe use of composts from sewage sludge in soil amending. The material must be free of toxic pollutants and pathogens. The European Union (UE) has fixed the requirements that compost must meet for its use in a safe mode [1]. The US-EPA has also regulated the use of compost and bio-soils [2]. However, the wide use of personal care products (PCPs) and other products related with human activities has led the contamination of this material with these new contaminants [3].

An accurate and sensitive method for the determination of selected EDCs in soil and compost from wastewater treatment plants is developed and validated. Five parabens, six benzophenone-UV filters and the antibacterials triclosan and triclocarban were selected as target analytes. The parameters for ultrasound-assisted extraction were thoroughly optimized. After extraction, the analytes were detected and quantified using ultra high performance liquid chromatography tandem mass spectrometry. Ethylparaben (ring–$^{13}C_6$ labelled) and deuterated benzophenone (BP-d_{10}) were used as internal standards. The method was validated using matrix–matched calibration and recovery assays with spiked samples. The limits of detection ranged from 0.03 to 0.40 ng g^{-1} and the limits of quantification from 0.1 to 1.0 ng g^{-1}, while precision in terms of relative standard deviation was between 9% and 21%. Recovery rates ranged from 83% to 107%. The validated method was applied for the study of the behavior of the selected compounds in agricultural soils treated and un-treated with compost from wastewater treatment plants. A lixiviation study was developed in both agricultural soil and treated soil and first order kinetic models of their disappearance at different depths are proposed. The application of organic composts in the soil leads to an increase of the disappearance rate of the studied compounds. The lixiviation study also shows the risk of pollution of groundwater aquifers after disposal or waste of these EDCs in agricultural soils is not high.

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P-ENV-12

Development of methodologies for the quantification of urinary metabolites of organophosphate and pyrethroid pesticides and its application in agricultural populations from Catalonia and Galicia

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Organophosphate (OP) and pyrethroid (PYR) pesticides are commonly used in agricultural applications as well as in domestic and gardening use. They have a strong potential to disrupt the brain and nervous system of insects and kill them. This neurotoxic effect is not highly selective and therefore these compounds are also toxic to other non-target species, including humans [1].

Once in the human body, OP and PYR pesticides are typically metabolized and excreted in urine within 4-48 hours after exposure, depending on the compound. Organophosphates are metabolized into dialkyl phosphates (DAPs) and specific compounds such as 3,5,6-trichloro-2-pyridinol, para-nitrophenol, malathion dicarboxylic acid and others. In the case of pyrethroids, several pesticides are metabolized into one single compound such as 3-phenoxybenzoic acid. In any case, the concentrations of pesticide metabolites in human urine vary depending on the exposure level [1]. Robust analytical methods are therefore needed for the study of these pesticides in urine as markers of the exposure of the populations to these pesticides.

Accordingly, two new analytical methodologies for the quantification of OP and PYR urinary metabolites have been developed taking into account the variability of concentrations found in human urines from both general and highly exposed populations from rural or agricultural sites. On the one hand, a fast and accurate high-performance liquid chromatography–tandem mass spectrometry (HPLC-MS/MS) method that allows the quantification of 9 biomarkers of several of these pesticides. On the other hand, a method based on GC-MS operating in negative chemical ionization (NCI) that has been applied for the first time in the quantification of DAPs in human urine.

These two methodologies are suitable for monitoring general and highly exposed populations because they provide high sensibility and low detection and quantification limits. Both methodologies have been externally checked out by participation in rounds of the German External Quality Assessment (G-equas) [2].

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P-ENV-13

LC-MS/MS and HRMS ANALYSIS OF ESTROGENS INCLUDED IN WFD

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The natural estrogens (estrone, E1; and 17β-estradiol, E2) or synthetic (17α-ethinyl estradiol, EE2) are excreted by humans or animals and introduced into environment through wastewaters. These compounds, considered as endocrine disruptors, have been included in the "Watch List of Water Framework Directive". Recently, in the Decision 2015/495/UE, an acceptable maximum level in method detection was set in 0.4 ng/L for E1 and E2 estrogens and 0.035 ng/L for EE2.

The objective of this study was to develop an analytical methodology for the determination of these estrogens in aqueous matrixes by LC-MS [1, 2]. The different steps of the methodology have been optimised: extraction, liquid chromatography and mass spectrometry. The limits of quantification obtained were 0.4 ng/L and the limits of detection were between 0.01 and 0.08 ng/L for the three estrogens.

Finally, several aqueous matrixes have been analysed: wastewater, superficial, underground and bottled water [3]. Only the natural estrogens, E1 and E2, have been quantified in wastewater matrixes in a level of ng/L. The compound E1 was found in a higher concentration than the compound E2.

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P-ENV-14

COMPARATIVE OF TWO EXTRACTION TECHNIQUES OF MICROCYSTINS IN SEDIMENT: ACCELARATED SOLVENT EXTRACTION/ULTRASOUNDS

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Cyanobacteria are prokaryotes, autotrophs and aerobic microorganisms. When input of nutrients is high into aquatic systems, it may generate eutrophication. The quantity of algae increases generating “blooms”. Blooms can be harmful to the environmental, animals and human health. The bloom decay consumes oxygen creating hypoxic conditions and increases the mortality of animals. Under favorable conditions of light of nutrients, some species of cyanobacteria could produce toxic secondary metabolites known as cyanotoxins, for instance saxitoxins or microcystins.

Cyanotoxins can be found in the water column and in the deeper layers of sediments due to the sedimentation cycle [1]. In the case of sediments, it is very important the process of extraction because it is the fundamental step to obtain reliable results.

In this study, sediment cores were collected from Las Conchas reservoir (Orense, Spain) to analyze microcystins MC-RR, MC-YR, MC-LR, MC-LA, MC-LY, MC-LW, MC-LF and MC-dmRR. These sediments have been extracted by ASE, which extraction rate is higher in comparison to other extraction techniques [2, 3], and ultrasounds. Wet and dry samples have been extracted with different proportion of eluents (methanol: water). Nodularine has been used as internal standard to evaluate the extraction efficiency.

Recoveries obtained from ASE are higher than ultrasounds method. Regarding to ASE, wet sample extraction are been more efficient than dry samples.

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P-ENV-15

ARSENIC SPECIES BIOMONITORING IN URINE FROM ADULT POPULATION OF ANDALUSIA

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Arsenic (As) in one of the most toxic elements to humans and its prolonged exposure, through consumption of water and food, can cause cancer and skin lesions. Inorganic forms of arsenic (arsenate (As (V)) and arsenite (As (III))) are more toxic while methylated forms (monomethylarsonate (MMA) and dimethylarsinate (DMA)) are considered only moderately toxic. In addition, other arsenic species, like arsenobetaine (AsB) and arsenosugars, show no toxicity. Therefore, the aim of this study is to determine which species of arsenic are present in bio-fluids such as urine, because they can provide information about detoxification mechanisms, which are triggered by the presence of this element and, of course, possible health impacts resulting from the consumption of arsenic containing food.

In the present study, analytical speciation of As has been carried out in 150 urine samples from Andalusia population. To this end, the methodology proposed by Contreras-Acuña et al [1] has been used, which is summarized as follows: urine is diluted (1:5) with HNO_3 5% (v / v) and As species present in the extract (As (V), As (III), MMA, DMA and AsB) are separated by liquid chromatography anion exchange (HPLC-AEC) coupled to an ICP-MS detector. The procedure has been validated using a reference material (ClinCheck® (level II)), which contained the studied species.

The results showed that most abundant As species in urine samples were: AsB>DMA>As(V)>As(III)>MMA, being AsB the most abundant (85 % of the total arsenic determined). This fact is very important because it demonstrated the absence of possible public health problems caused by the feeding of Andalusian population, due to the innocuous nature of AsB. As relevant details, it can be remarked that the Andalusian province whose population had the highest concentration of total As in urine is Málaga, while Córdoba present the lowest concentration.

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Acknowledgements: This work was supported by the project CTM2015-67902-C2-1-P from the Spanish Ministry of Economy and Competitiveness (MINECO), and by projects P12-FQM-0442 from the Regional Ministry of Economy, Innovation, Science and Employment (Andalusian Government, Spain). Finally, authors are grateful to FEDER (European Community) for financial support, Grant UNHU13-1E-1611.

P-ENV-16

COMPARING CHROMATOGRAPHIC DATA FOR SOIL LIPID COMPOUNDS AS DENSITY SURFACES IN THE SPACE DEFINED BY THEIR ATOMIC RATIOS

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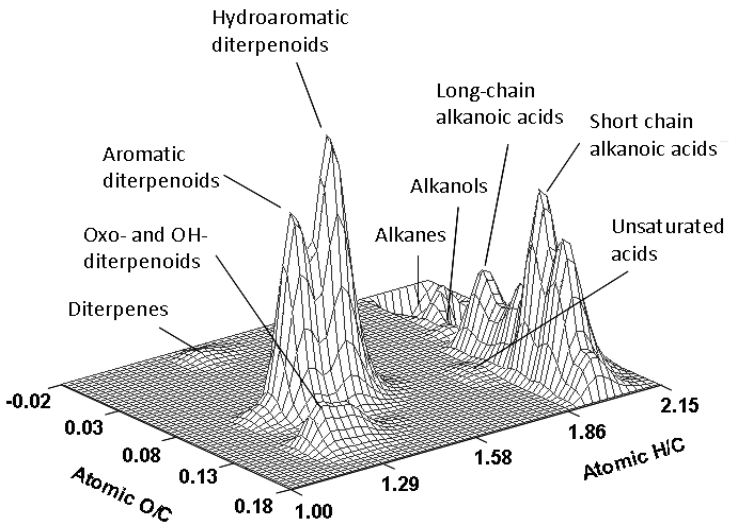
Soil lipids from undisturbed forests (*Quercus rotundifolia*) are compared with those of adjacent sites affected by i) clearing, ii) cultivation, iii) wildfire and iv) reforestation (*Pinus pinea*). The methylated lipids from 16 soils extracted with petroleum ether (40–70°C) were analysed using an OV-1 capillary column into an HP 7890A gas chromatograph coupled to a 5975C quadrupole mass detector, using ethylvanillin as internal standard.

Lipid composition data were examined from an unconventional exploratory approach in which total abundances of the individual compounds are displayed as *z* axis on a plane corresponding to the classical Van Krevelen (1950) plot [1] with atomic H/C and O/C ratios as coordinates. After applying a moving average algorithm to the cumulative values per unit area, the resulting interpolated 'surface density plots' display well-defined, 3D-peaks corresponding to unsupervised clusters of compounds with similar stoichiometry. Additional 'subtraction surfaces' were calculated from data pairs of compounds from disturbed soil minus those from the control soil multiplied by a suitable factor from the known differences in lipid concentration per soil weight. These subtraction surfaces show positive and negative values depending on either the environmental perturbation has lead to inputs or losses of specific compounds (i.e., its degradation, exportation, diagenetic transformation, or condensation into macromolecules…). Positive lipid balance was typical in soils affected by wildfires, with preferential accumulation of diterpenoidal compounds such dehydroabietin and simonellite, as well as in soils after reforestation (Fig.: soil under *Q. rotundifolia* reforested with *P. pinea*). Subtraction surfaces with profound negative valleys illustrate heavy depletion of long-chain aliphatics (as in cleared forests which, however, may incorporate cyclic compounds such as triterpenes (e.g., friedooleans in soils under angiosperm vegetation, norambreinolid-type diterpenes in cultivated soils), or steroids in the pasture site).



In general, the higher complexity of the surfaces in disturbed soils than in virgin soils could be reflecting that preexisting molecules from the original lipid signature still coexist with new lipids introduced by the change of soil use.

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P-ENV-17

DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN WATER SAMPLES BY USING MATERIALS CONTAINING BOUNDED CYCLODEXTRIN IN SOLID-PHASE EXTRACTION

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Solid-phase extraction is one of the most important techniques for sample purification and concentration. In fact, a wide variety of solid phases have been used for sample preparation over time. In this work, the efficiency of new microporous solid-phase adsorbents made from modified cyclodextrin bounded to a silica network, is evaluated through an analytical method which combines solid-phase extraction with high-performance liquid chromatography to determine polycyclic aromatic hydrocarbons in water samples.

Several parameters that affected analytes recovery, such as the cyclodextrin type, the amount of solid phase, the pH, the nature and volume of the eluent or the sample volume and concentration influence have been evaluated. Experimental results indicate that materials containing both β-cyclodextrin [1] and ɣ-cyclodextrin possess adsorption ability to the tested analytes. Moreover, recovery results improve those obtained in previous studies using an included cyclodextrin-silica material [2] for the solid-phase extraction of polycyclic aromatic hydrocarbons.

Furthermore, quantification limits rounded 1-4 μg L^{-1} and fine linear correlations between peak area and concentration were found in the 1.3-100 μg L^{-1} range under the optimum conditions. Developed methods have good repeatability and reproducibility, with coefficients of variation under 10 %, approximately. Due to the preconcentration results, this material may represent and alternative for trace analysis of polycyclic aromatic hydrocarbons in water through solid phase extraction.

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P-ENV-18

COMPARATIVE EFFECTS OF SEVERAL CYCLODEXTRINS ON THE EXTRACTION OF POPs FROM CONTAMINATED SOILS AND SEDIMENTS

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Soil and sediment contamination due to industrial and urban discharges are creating great concern particularly in the vicinity of areas with high population. Many chemicals from waste discharges become associated with soils and sediments, which could act as a sink of organic contaminants. Therefore the management of urban and industrial solid wastes is now a matter of high priority.

The objectives of the present study were: (i) to thoroughly characterize the contaminated soils and sediments to determine their contaminants content, and (ii) to evaluate the abilities of a natural CD (β-cyclodextrin, BCD) and three chemically modified CDs (2-hydroxypropyl-β-cyclodextrin, (HPBCD), randomly methylated-β-cyclodextrin (RAMEB) and hydroxypropyl-γ-cyclodextrin (HPGCD)), to extract as much contaminants as possible. Cyclodextrins (CDs) have been recently proposed as a non-toxic and biodegradable alternative to organic solvents and surfactants because they have the ability to increase the apparent water solubility of low-polarity organic compounds [1] (Morillo et al., 2012), reducing their sorption and facilitating their transport through soil [2] (Sánchez-Trujillo et al., 2014).

We have evaluated the performance of such approach in 3 case studies: (i) soils contaminated with polycyclic aromatic hydrocarbons (PAHs) from a mine in Oviedo; (ii) soils contaminated with creosote from a railway sleeper old deposit; (iii) sediments from Flix contaminated with Persistent Organic Pollutants (POPs). Soils and sediments were extracted using solid-liquid extraction and were characterized by gas-chromatography coupled to mass spectrometry (GC-MS). After the initial contaminant concentration and contaminant profile was identified, non-exhaustive extraction of contaminants from soil/sediments using an electrolyte solution and aqueous CD solutions was undertaken in sequential batch experiment and a high potential for recovering PAHs and POPs from contaminated solid wastes was observed. Thus, the procedure herein proposed is capable to remove contaminants from soils and sediments.

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P-ENV-19

PERSISTENCE OF SOIL ORGANIC MATTER AS A FUNCTION OF ITS MOLECULAR COMPOSITION AS REVEALED BY Py-GC/MS

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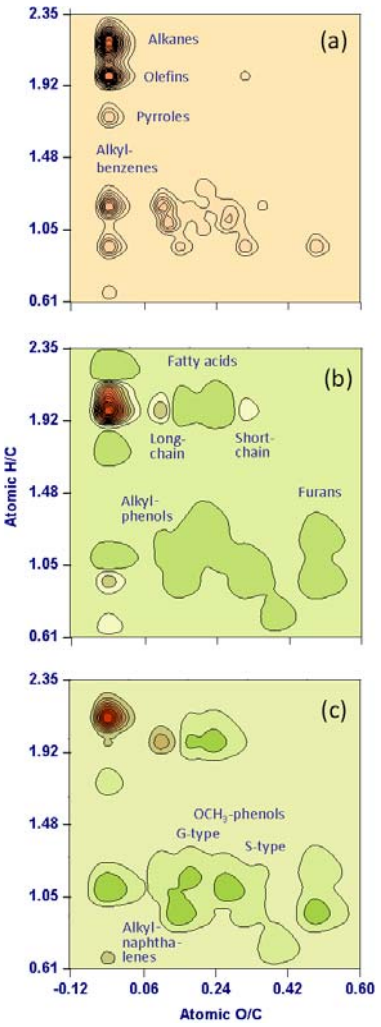
There is a large controversy on whether the resilience of soil organic matter (SOM) depends on physical protection by soil minerals or on its intrinsic molecular composition [1]. In the case study of 30 volcanic soils from Tenerife (Spain), the dependent variables (DV) were total amount of SOM and TMC (total mineralization coefficient, CO_2 released under incubation). This research focuses on estimating DVs using SOM molecular descriptors obtained by pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) using a Pyrojector® device (SGE instruments) on a GC/MS Finnigan Trace GC Ultra, a Trace DSQ MS and an HP-1 column. Up to 47 of the 102 major Py compounds were selected as descriptors (independent variables, IVs) attending to its normal distribution and few missing values.



The relationships between DVs and normalized GC peaks (IVs) were examined by three approaches: **(a)** Partial least squares regression (PLSR) checking different pretreatments (standardization of IVs as total or relative abundances, mean centering, variance scale, and logarithmic or square root transformations). Spurious models were discarded after repeating PLSR models with the randomized DV; **(b)** Pearson's correlation coefficients between each DV and the 47 IVs; comparison with other indices computed during PLSR: the variable Importance in the projection (VIP), *b* coefficients, *W* weights and factor loadings [2]; **(c)** comparing soil subsets representing opposed levels of the DVs: The 30 soils were ordered in decreasing DVs values and two subsets were considered, e.g., above *vs* below the median of the DV (or in the uppermost Q1 quartile vs Q4), i.e., soils 'behaving as C-sinks' *vs* 'soils with 'poor C sequestration potential'. Differences between subsets were checked by ANOVA and plotted as subtraction values.

The results from PLSR demonstrated that both SOM concentration and TMC can be predicted ($P< 0.05$) from the relative abundance of 47 major pyrolysis compounds. Although no cause-to-effect is inferred from this fact, it makes evident that SOM molecular composition differs in terms of its resistance to biodegradation. For rapid perceptual identification of the results, the indices for the IVs: VIPs **(a)**, Pearson's r^2 **(b)**, average differences between DV subsets **(c)**, were represented in the *z* axis in 3D plots (as contour plots, in the figure) the coordinates in the basal plane being atomic H/C and O/C ratios of the Py compounds in a classical Van Krevelen diagram [3]. Applying a moving average algorithm to *z* values, we obtain clusters (showing gradients of compounds with similar stoichiometry) in some way illustrating structural domains of the SOM (carbohydrate-and lignin-derived, condensed lipid…).

The figure illustrates the structural components prevailing in C-depleted and in C-rich soils (– or + values shown in red and green, respectively, for **b** & **c** approaches). In the case of the VIPs **(a)**, which is a positive index, previous checking of **b** or **c** plots is required for its complete interpretation. The 3 approaches coincided in pointing out that the SOM levels parallel the accumulation of lignin- and carbohydrate-derived structures, and the depletion of condensed polyalkyl structures; in other words, the larger the quantity, the lowest the quality of the SOM in our soils. Practically the same pattern, but with signs swapped, was obtained for the TMC.

Judging the approaches (**a**–**c**) in terms of workload and time consumed, and despite PLSR is frequently invoked to have outstanding potential to extract underlying information, we found approach (**c**) the most simple and intuitive. In the other cases, IVs with VIPs> 1 were not always correlated ($P< 0.05$) with the corresponding DV or, in the case of Pearson's coefficients, careful control of outliers is required.

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[3] D.W. Van Krevelen, *Fuel* **29** (1950) 269–284.

P-ENV-20

ANALYTICAL PYROLYSIS (Py-GC/MS) FOR RAPID MONITORING OF SOIL ORGANIC MATTER RECOVERY IN A CHRONOSEQUENCE OF SEMIARID MEDITERRANEAN BURNED FORESTS

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Wildfire is a frequent environmental perturbation in Mediterranean ecosystems, which severely affects physical and chemical soil properties. In particular, the composition and properties of soil organic matter (SOM) are those experiencing the most important transformations. In the short term, most fire-induced alterations frequently contribute to the loss of soil quality and productivity. For these reasons, post-fire soil management requires local information about the natural post-fire evolution of the different soil types. Most recent studies have focused on the effects of fire in SOM composition, but research about progressive changes in the course of the restoration is scarce. In August 2012, a wildfire affected a forest area of *ca.* 90 ha in Montellano (Seville, SW Spain). The predominant vegetation consisted of *Pinus pinaster*, *Pinus halepensis* and *Eucalyptus globulus*. Soil samples were collected 1 month and 25 months after the fire. Sixteen months after the wildfire heavy machinery was used to remove burnt trees and plant residues as part of the post-fire rehabilitation practices.

The analysis of SOM molecular composition was done using analytical pyrolysis (Py-GC/MS), i.e., a versatile on-line analytical facility which requires no sample pretreatment. Pyrochromatograms of whole soil samples collected 2 years after the fire showed that SOM was still altered by fire, i.e., soil couldn't be considered as restored. The evolution was illustrated by an improved Van Krevelen's graphical-statistical method, where the fire damage levels—or the soil recovery status—were visually compared as surface density plots in the space defined by compound-specific atomic H/C and O/C ratios of the Py-GC/MS molecules, either as autocumulative total abundances, or after subtracting the values at the different stages of the chronosequence.

Our results indicate that rehabilitation practices carried out after the fire, which included the removal of burnt vegetation, far from helping soil recovery may have resulted into delayed soil recovery. In addition, the mechanical disruption of topsoil by heavy machinery used enhanced erosion risks. Analytical pyrolysis could be an important tool for the continuous monitoring, at a molecular level, of SOM evolution with time.

P-ENV-21

PHOTODEGRADATION OF UV FILTERS IN THE AQUATIC ENVIRONMENT BY ADVANCED OXIDATION PROCESSES FOLLOWED BY SOLID-PHASE MICROEXTRACTION-GAS CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY

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The final fate of organic UV filters is the aquatic environment due to their direct entrance from bath areas of lakes or beaches and domestic and recreational discharges such as swimming pool waters, since these compounds are employed in daily personal care products including sunscreen products. Organic filters are considered as emerging pollutants and their behavior and (eco)toxicological effects are not well known. One of them, the 2-ethylhexylmethoxycinnamate (2EHMC) has been recently integrated in a Watch List for the purpose of supporting its future prioritization in surface water [1].

The aim of this work is the simultaneous degradation of multiclass organic UV filters, including the 2EHMC in different types of waters. Different radiation sources were tested in order to obtain the best conditions for the degradation efficiency. Other approaches such as the use of catalysts to improve the removal rate were also studied.

Samples were mainly analyzed by HS-SPME followed by GC-MS/MS and under the best experimental conditions, different natural and recreational waters were irradiated into lab-scale photoreactors showing efficient removal for most of the studied analytes.

This research was supported by FEDER funds and projects GPC2014/035, and CRETUS (AGRUP2015/02) (Xunta de Galicia) and CTQ2013-46545-P (Ministry of Economy and Competitiveness, Spain). M. Vila acknowledges Ministry of Education, Culture and Sport for a FPU grant. This work was also financially supported by Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER funds through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI)–and by national funds through FCT - Fundação para a Ciência e a Tecnologia). V.J.P. Vilar acknowledges the FCT Investigator 2013 Programme (IF/00273/2013). F.V Hackbarth acknowledges her postdoctoral fellowship provided by CNPq (Process: 203598/2014-8).

[1] Commission Implementing Decision (EU) 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council, in Off. J. Eur. Union, L78/40, 2015.

P-ENV-22

A CHIRAL METHODOLOGY BY CD-MEKC TO STUDY THE TOXICITY OF BIOALLETHRIN ENANTIOMERS ON NON-TARGET ORGANISMS

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Pesticides in general and especially insecticides are considered the most important group of environmental pollutants due to their widespread use worldwide. About 25% of them are chiral and this fact has important implications both in their biological activity and degradation patterns. A rigorous evaluation of environmental risk due to the presence of pesticides in environment needs a revision of toxicity data reported. More attention should be paid on the non-target organisms, and considering the chiral nature of most of these compounds, the impact of enantiomers must be studied more in deep, considering diffuse contamination, mobility and bioaccumulation of pollutants. Toxicity of these micropollutants has scarcely been studied on non-target organisms, especially in terrestrial environments.

Bioallethrin ((RS)-3-alyl-2-methyl-4-oxocyclopent-2-enyl(1R)-trans-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate) is a synthetic pyrethroid insecticide bioaccumulative, persistent in soil and slowly degradable in the environment. Studies in animals demonstrated that it is a central nervous system stimulant and there are evidences that the S enantiomer of bioallethrin causes severe damage to blood immunocompetent cells. However, toxicity studies on non-target organisms have not been reported.

In this work, a chiral methodology by micellar electrokinetic chromatography with cyclodextrins (CD-MEKC) was developed to evaluate the toxicity of the optical isomers of bioallethrin, on the growth of the unicellular freshwater green alga *Pseudokirchneriella subcapitata* and on the germination of the higher plant *Sorghum bicolor*. The use of sodium deoxycholate bile salt and acetyl-β-CD enabled the separation of bioallethrin enantiomers with a high enantioresolution (7.4) in a short analysis time (6.5 min). The analytical characteristics of the developed method were evaluated in terms of linearity, accuracy, precision, and limits of detection (LOD) and quantitation (LOQ). Different toxic responses and bioaccumulation profiles were found for each organism.

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P-ENV-23

STUDY OF GEL PERMEATION CHROMATOGRAPHY TO PURIFY FOOD EXTRACTS FOR DETERMINATION OF PERSISTENT ORGANIC POLLUTANTS

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Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) are included in the group of persistent organic pollutants (POPs) due to their properties (persistence, bioaccumulation in lipids, transboundary transport and toxicity). Other compounds, such as organochlorine pesticides, polybrominated diphenyl ethers or Dechlorane Plus, share the same properties as PCDD/Fs and PCBs. Bioaccumulation in lipid tissues and biomagnification in the food chain make exposure through food important for humans. Therefore, the analysis of these pollutants in food is essential for the evaluation of that exposure.

The main steps for the determination of persistent organic pollutants in food items are: (1) addition of extraction internal standards to the sample, (2) extraction, (3) clean-up, (4) concentration and addition of syringe standards, (5) instrumental determination by GC-HRMS and (6) quantitation by the isotopic dilution method.

In this work, we have focused on the study of the clean-up step, based on gel permeation chromatography (GPC). In order to separate the analytes from the fat, Bio-Beads S-X3 resin was used as stationary phase. The elution was performed with a mixture of dichloromethane and hexane (1:1). The elution profile of the analytes was studied loading a standard solution of a mixture of the pollutants of interest on the GPC column and collecting and analysing different fractions separately by GC-ECD. The results showed that the analytes were not eluted in the first 150 mL but in the following 75 mL. Since the objective of the work was the clean-up of food extracts, the same study was carried out with vegetable oil. Elution profile was very similar to that obtained with the standard solution. Recoveries of the pollutants were high (90-100%).

GPC clean up step was included in the general procedure for the analysis of PCDD/Fs and PCBs, both dioxin-like PCBs and non dioxin-like PCBs, in paprika samples. It was verified that the technique was not only useful to obtain appropriate clean extracts for the instrumental determination, but also to eliminate other purification step, such as Florisil columns. The accuracy and precision were evaluated and they were in the range required by the European regulations.

P-ENV-24

HOLLOW-FIBER LIQUID PHASE MICROEXTRACTION GAS CHROMATOGRAPHY TANDEM MASS SPECTROMETRY FOR THE DETERMINATION OF PHTHALATES IN WATER SAMPLES

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Phthalic acid esters (PAEs), also known as phthalates, are commonly used as plasticizers in plastic products manufacturing in order to improve their properties. The analysis of PAEs in plastic-packaged food and beverages has become a very important issue in the last years since they can migrate to the surrounding environment. In fact, it has been demonstrated that a continuous human exposure to these compounds can lead to serious health problems [1].

Concerning sample pretreatment, liquid-phase microextraction (LPME) techniques have come up as an alternative to previous procedures in order to miniaturize and simplify the process. Different modes in which this method can be developed, single-drop microextraction (SDME), hollow-fiber LPME (HF-LPME) and dispersive liquid-liquid microextraction (DLLME), make possible to carry out analytes extraction and concentration in a single step. In particular, HF-LPME, developed in 1999 by S.-P. Bjergaard et al. [2], show important advantages such as simplicity of operation, low cost and high enrichment factors, among others. However, and despite the excellent advantages of this sample preparation method, it has hardly been applied for the determination of PAEs in water samples.

In this work, a HF-LPME methodology has been used for the extraction of 16 PAEs (i.e. dimethyl phthalate, diethyl phthalate, dipropyl phthalate, di-isobutyl phthalate, dibutyl phthalate, bis (2-methoxyethyl) phthalate, bis-isopentyl phthalate, bis-2-ethoxyethyl phthalate, bis-n-pentyl phthalate, butyl benzyl phthalate, bis-2-n-butoxyethyl phthalate, dicyclohexyl phthalate, di-(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate, diisononyl phthalate, diisodecyl phthalate) and a substitutive of the DEHP (bis (2-ethylhexyl) adipate) from different water samples. The developed methodology was validated for several aqueous matrices obtaining limits of detection in the low µg/L range.

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P-ENV-25

Comparative study of three extraction methods for the analysis of organophosphate flame retardants in soil and biota

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Organophosphate flame retardants (PFRs) are diverse group of chemicals added to manufacture materials to inhibit or delay the spread of fire. They are also used as plasticizers, stabilizers, antifoam, humectants, etc. The fact that they usually are not chemically bonded to the material, together with the large volumes consumed and its wide range of applications, raise high concern about the concentrations than they can reach in the different compartments of the ecosystems. Few methods are available for comprehensive PFRs detection in biota and soil, therefore, a comparative study of three extraction methods for the determination of 11 PFRs in soil and biota was performed in order to select the one that provides the best recoveries and the highest sensitivity. European eel (*Anguilla Anguilla*) and rainbow trout (*Oncorhynchus mykiss*) were used for biota analysis. The soil was obtained near the Turia River in Valencia. The determination of PFRs was made by high-pressure liquid chromatography-tandem mass spectrometry (HPLC-MS/MS). The compared methods were based on solid-liquid extraction (SLE) with [1] an aqueous solution of ethyl acetate and acetonitrile, [2] methanol and [3] a mix of dichloromethane and hexane. The best recoveries for biota analysis were obtained with the method based on methanol, 70-116% for European eel and 47-122% for rainbow trout. For soil analysis, both aqueous solution of ethyl acetate and acetonitrile (65-90%) and methanol (60-121%) provided appropriate recoveries.

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P-ENV-26

ASSESSING DRUGS OF ABUSE DISTRIBUITON IN TURIA RIVER BASED ON GEOGRAPHIC INFORMATION SYSTEM AND LIQUID CHROMATOGRAPHY MASS SPECTROMETRY

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Until now, emerging contaminants, including drugs of abuse, have been found in many Spanish rivers, such as, Ebro, Jucar, Guadalquivir and Llobregat [1,2]. In this study, samples of water and sediments were collected by fieldwork. The content of drugs of abuse with ultra-high performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) was examined. Combining the fuzzy membership functions, maximum entropy modeling and geographical information system (GIS), the suitable range of each factor affecting attenuation and spatial distribution of these compounds were assessed.

A total of 42 drugs of abuse and metabolites that belong to amphetamines, tryptamines, piperazines, pyrrolidinophenone, arylcyclohexylamine, cocainics, opioids and cannabinoids groups were monitored. Sampling campaign was carried out in 2 periods in 2012 and 2013. There were 22 sampling sites in 2012 and 31 in 2013 distributed along the river. These compounds were extracted from 250 mL of water by solid phase extraction and determined by liquid chromatography triple quadruple mass spectrometry using an electrospray ionization source in positive mode.

The method detection limits ranged from 1 to 30 ng L^{-1} and the recoveries from 31 to 125 %. The monitoring of these compounds in the Turia River Basin was plotted using Geographic Information System (GIS) software in combination with a demographic scan statistic to generate risk maps of illicit drugs and identify clusters of product- and compound-specific abuse.

The highest presence of drugs of abuse in Turia River Basin were those belonging to cocainics group (benzoylecgonine 40.1 % up to 76.8 ng L^{-1} in 2012 and 25.8 % up to 12.7 ng L^{-1} in 2013) and opioids group (methadone 13.6 % up to 39.3 ng L^{-1} in 2012 and 22.6 % up to 40.1 ng L^{-1} in 2013). These results illustrated the pollution status by illicit drugs of the Turia River Basin, which is more contaminated in the lower part of the river. These results were expected since population is much more concentrated in the lower part of the river near to the sea. Anyway, a better understanding of local risk distribution may have implications for response strategies to future.

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P-ENV-27

THE EFFECT OF FIRE ON LIPID COMPOSITION OF SOIL SIZE FRACTIONS AND SOIL HYDROPHOBICITY

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Low soil-water affinity and soil water repellency (SWR, hydrophobicity) prevents water from wetting or infiltrating soils in burnt and unburnt ecosystems, triggering hydrological, geomorphological, geochemical, and biochemical changes. Fire may destroy, develop or even enhance SWR in previously wettable or water-repellent soils. SWR is partially due to a lipid-like cover, rich in fatty acids (FAs). Here we report the first results of a study on the effect of fire on the distribution of soil lipids and their role in the SWR. Two samples of sandy soil under Quercus suber canopy at the Doñana National Park (SW-Spain) were taken. One come from a burnt site and the other from an adjacent unburnt (control) one, with the same physiographic characteristics. SWR was determined using water-drop-penetration-time test in the <2 mm sieved (bulk) soils and in six size fractions: 1-2 mm, 0.5-1 mm, 0.25-0.5 mm, 0.1-0.25 mm, 0.05-0.1 mm and <0.05 mm. Lipids were extracted from all samples (n = 14); the FAs and neutral lipids were identified and quantified by GC/MS and GC/FID. The carbon isotope ratios ($\delta^{13}C$ values) for the individual fatty acids were determined by GC/C/IRMS.

The SWR values of soil samples and fractions were statistically different (p < 0.01), for both, the fire-affected and control soils, and different grain-size fractions. SWR values in burnt bulk soil and 0.05-0.1 mm fraction were higher than in unburnt homologues. The coarsest and finest soil fractions (1-2 mm and <0.05 mm, respectively) of the unburnt soil were the most hydrophobic; in contrast, the finer fractions (0.05-0.1 mm and <0.05 mm) were the most hydrophobic in burnt soils. The total amount of lipids and total FAs were higher in burnt bulk sample and all the size fractions, except the coarser one, which had twice the amount of lipids, compared to the burnt one. All samples showed a similar distribution of saponifiable lipids, characterized by straight-chain saturated acids in the C_{14}-C_{32} range and only differing in their relative abundances. In bulk soil and <0.5 mm fractions the concentrations (in µg FA/g soil) of the FAs were higher in burnt compared to the unburnt soil (this difference was small or absent in C_{22}). For the coarser fractions, the opposite trend was observed in most FAs, except C_{18}, and in the 0.5-1 mm fraction for $C_{<20}$ acids. Principal component analysis (PCA) performed on lipid concentration, concentration ratios, and SWR indicated that hydrophobicity of soils was positively correlated to total amount of lipids, normal $C_{>24}$ FAs and branched $C_{>24}$ FAs, and negatively correlated with the even/odd FAs ratio. The biosynthetic origin of these lipids and their transformation pathways during a fire will be discussed with the results of the ongoing measurements of the $\delta^{13}C_{FA}$ values.

P-ENV-28

QUANTITATIVE GC-MS ANALYSIS OF FREE LIPIDS FROM PINE AND JUNIPER LEAVES, LITTER AND SOILS

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Soil lipids consist of a complex heterogeneous mixture of a wide variety of compounds non-soluble in water, but soluble in organic solvents. Most of lipids derive from plant residues, microfauna and soil microorganisms and constitute only a small proportion of the soil organic matter. However, it is considered that they display an important influence on many soil processes and properties; hence lipids could be considered as diagnostic molecules for characterizing the structure and dynamics of different ecosystems [1]. Scarce information regarding biogeochemical fate in soil of the free lipid fraction is available in literature and the only existing data are not quantitative. Thus, in the current work, a comprehensive quantitative study of lipid composition of leaves, litter and soils of *Juniperus communis* (common juniper) and *Pinus sylvestris* (Scots pine) has been performed.

Samples were extracted with dichloromethane. The GC-MS analyses of the extracts were performed using a capillary column coated with methylsilicone as stationary phase. In a first stage, a series of compounds were checked to be used as internal standards. The best results regarding accuracy and reproducibility were obtained using 1,2-diphenyl-1,2-ethanedione, which was selected for subsequent studies.

While litter extracts presented the widest compound diversity (155 and 136 compounds identified in juniper and pine litter, respectively), leaf extracts showed the highest lipid concentrations (5.6 mg g^{-1} juniper leaves and 7.3 mg g^{-1} pine leaves). Only 47 lipid compounds were detected in pine soil; this sample also showed the lowest lipid concentration (0.08 mg g^{-1}).

The molecular composition of the free lipid fractions underwent diagnostic changes in the course of its transformation from leaves to soil. Overall, the lipid extracts from leaf and litter samples were dominated by terpenoids while alkanes were the main compounds in soil extracts. It is worth to note that alkanes higher than C_{20} were more abundant in juniper leaves (0.6 mg g^{-1}), while those with less than 20 C atoms were more abundant in juniper soil (0.2 mg g^{-1}). In general, monoterpenes were less abundant than sesquiterpenes and diterpenes.

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PJ-ENV-29

DEVELOPMENT OF AIR SAMPLERS BASED ON CYCLODEXTRIN-SILICA COMPOSITES FOR ENVIRONMENTAL ANALYSIS

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Sampling of organic pollutants in air presents great difficulties due to their low concentrations in this medium. In this work, the efficiency of materials based on silica structures containing bounded cyclodextrin, specifically β-cyclodextrin and ɣ-cyclodextrin, has been evaluated in order to sample and preconcentrate phenolic compounds in air.

In this way, variables affecting retention and extraction of phenol, o-cresol, m-cresol, p-cresol, guaiacol, vinylphenol, methoxyvinylphenol, ethylphenol, ethylguaiacol and eugenol have been studied and the quantitative determination of analytes has been performed using reverse-phase high resolution liquid chromatography. Results indicate that the studied materials are suitable for air sampling, being important to highlight the use of the bounded β-cyclodextrin material, whose recoveries were between 83 % and 95 %. It seems important to highlight that this new bounded cyclodextrin phase improved recoveries obtained for a previously studied included cyclodextrin material, specifically for vinylphenol and methoxyvinylphenol analytes [1]. By contrast, lower recoveries were obtained using the solid phase containing bounded ɣ-cyclodextrin, with recovery values rounding 65 %.

Regarding method analytical parameters, it seems important to stand out its repeatability, whose coefficients of variation using the β-cyclodextrin material were below 4 % for intra-day analysis and under 15 % for inter-day analysis. Moreover, vinylphenol has a 20 times worse sensitivity than the rest of the studied analytes.

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P-ENV-30

STUDY OF SILICA-STRUCTURED MATERIALS FOR ORGANOPHOSPHORUS PESTICIDES SAMPLING AND DETERMINATION

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Pesticides are a wide group of chemicals whose toxicity is one of their most important properties. Nowadays, the use of organophosphorus pesticides is widespread and, for this reason, their control and vigilance is usually required. In this work, the efficiency of diverse solid phases based on silica structures, belonging both to xerogel and UVM-7 material families, has been evaluated for sampling and preconcentrate these analytes and for their later determination by gas chromatography.

For this purpose, synthesized materials have been first characterized and then several parameters that affected organophosphorus pesticides recovery through retention and extraction conditions have been optimized. In this way, a new method for the determination of ethoprophos, diazinon, chlorpyrifos-methyl, tolclofos-methyl, fenitrothion, malathion and chlorpyrifos in air has been developed.

Experimental results indicate that the Ti-UVM-7 material is an alternative for the most commonly used solid phases (XAD-2). Quantitative recoveries between 82 % and 108 % have been obtained for all analytes following the developed method. Moreover, acceptable limits of quantification have been reached under the optimum conditions and good linear correlations in the 0.02-10 µg mL^{-1} range have been achieved. In relation to method repeatability, coefficients of variation present values under 13 %. For these reasons, the possibility of using this new solid phase for environmental analysis has been proved.

P-ENV-31

ANALYTICAL PYROLYSIS (Py-GC/MS) OF SEDIMENTS: SEA-LEVEL RISE EPISODES DURING THE HOLOCENE IN THE POTENGI–JUNDIAI ESTUARY, NE BRAZIL

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Understanding sea-level changes on various time-scales is important because it is usually associated to climate changes [1]. Sediments in estuaries may retain a continuous record of climatic and environmental markers surrogated to factors like relative sea level (RSL), vegetation cover, and connectivity with the open ocean. Sediments accumulated since the last glacial maximum (LGM; *c.* 20 kyr.) are particularly informative and encompass valuable information to infer accurate RSL curves. Lipid biomarkers are preserved in sediments and include molecular markers like *n*-alkanes and *n*-alkanoic acids increasingly used for paleoclimate and paleoenvironmental reconstructions [2]. In this communication analytical pyrolysis (Py-GC/MS) is used to study the structure of organic matter (OM) contained in dated sediments from core IG-8 (31 m depth). This technique has been previously used to monitor past environmental changes in the area [3]. The core was drilled in the area of central flood delta of Potengi-Jundiai estuary, through the sedimentary sequence accumulated since ca 9,8 kyr cal BP [4]. Marked compositional differences between the OM of different ages were found. Specifically the *n*-alkane series were found particularly informative in discriminating OM sources (terrigenous vs marine).

In the surface, the alkane series is characterized by a high average chain length (ACL) value indicating a clear influence from terrestrial vegetation. From 6.5 to 11.5 m depth an increase in the terrigenous contribution is observed by an increase in ACL values in correspondence with $\delta^{13}C$ depletion. At 22.8 m depth and at 26.6 m there are again inputs from terrestrial plants, but for short periods of time. Bellow 26.6 m the influence is marine and ends at 29.45 m with a neat alteration of sediment isotopic signature with a $\delta^{13}C$ enriched layer with no organic markers and indicating the occurrence of sedimentary conditions favouring carbonate formation. Below this depth, the OM in the sediments shows a conspicuous terrestrial influence (depleted conductivity and $\delta^{13}C$ and increase in alkanes ACL and long vs short chain length (L/S) ratio) that increase towards bottom of the core down at 30.95 m. This possibly indicates a drastic sea-level change during this period of time.

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P-NDI-1

CHARACTERIZATION OF PLASMA PROFILES IN NEGATIVE IONIZATION MODE WITH DIFFERENT CAPILLARIES FOR CE-MS

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Capillary Electrophoresis (CE) is a well suited separation technique for the analysis of aqueous samples as biofluids and it offers the opportunity to detect polar and ionic compounds sometimes overlooked with other techniques [1] being a complementary tool for multiplatform analysis. Up to now described CE-MS methods for metabolic fingerprinting are mainly based on positive MS detection, while MS detection in negative mode will permit to obtain more complete metabolite profiles.

Soga and col. have developed a well-known CE-MS method for the analysis of anionic metabolites with reverse polarity, with cationic coated capillaries (COSMO (+)) for negative MS detection [2]. Non-covalently bonded coated capillaries with triple layer “PB-DS-PB” polybrene (PB), dextran sulfate (DS) and PB have been used [3]. However, MS contamination is always a risk in this type of conditions.

Nowadays, application of CE-MS for large number of samples and long-term metabolic studies should be proved in terms of migration time and peak area reproducibility, but also compatibility with the MS detector.

Our aim is developing robust protocols for neutral and anionic compounds in metabolomics studies not depending on unknown buffers or leaking capillaries and for that and we have explored new coatings and their applicability in metabolomics. We want to use capillaries with known and stable coatings but new in metabolomics. New coating that can eliminate electroosmotic flow (EOF) as poly vinyl alcohol (PVA) or polyethylene oxide (µ-WAX) will be included in a first stage but also capillary columns chemically bonded, classically used for GC-MS, as µSil-DB-1 are being tested to explore their possibilities in CE-MS for untargeted analysis.

A reference plasma material (RSM 1950) which is intended to represent a “normal” plasma with certified and/or reference values for many metabolites will be used in addition to pure standards to evaluate the number of compounds that are identified and their reproducibility.

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P-NDI-2

SIMULTANEOUS DETERMINATION OF SEMIVOLATILE DBP IN DRINKING WATER SAMPLES BY LIQUID PHASE MICROEXTRACTION AND GAS CHROMATOGRAPHY-MS/µECD

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In the last decades, the chemical disinfection of drinking water has allowed to reduce significantly the incidence of infectious waterborne disease, but reactions of disinfectants such as chlorine with natural organic matter contained in source waters produces chemical mixtures of different undesirables compounds considered disinfection byproducts (DBPs). More than 600 of these compounds have been identified in drinking water and this number continues growing. Exposure to DBPs can occur throughout the lifetime via multiple pathways, such as oral intake via, and inhalation through breathing and dermal contact by the skin during regular indoor activities, such as showering, bathing and cooking, which represent important risks to human health. Until now, most studies have been focused on trihalomethanes (THMs) and haloacetic acids (HAAs) analysis, but there is a considerable uncertainty over the identity and levels of other DBPs that can affect the population through drinking water. Therefore, there is a need for comprehensive quantitative occurrence and toxicity data to determine whether other DBPs have present and represent health risk.

In this study, a novel hollow fiber liquid phase simultaneous microextraction method has been performed for the first time and applied to pre-concentrate 20 semi-volatile species of DBPs, including, 4 Thrihalomethanes (THMs), 7 Halonitromethanes (HNMs), 6 Haloacetonitriles (HANs), 3 Haloketones (HK). The extraction process was previously optimized considering different configurations of hollow fiber for direct extraction and headspace. The most significant variables affecting the extraction such as acceptor solvent, temperature, and time, length of fiber, adding of salt, stirring speed and pH were optimized. The extraction was performed in only one step, with 2 pieces of hollow fiber (Accurel Q3 / 2, 0,6µm). 20 µL of each extract obtained were collected into a 1.5 mL vial attached to 250 µL insert. Finally, 1 µL was injected into the GC-µECD/MS system. The extractions were carried out during 30 min at 45 °C and 700 rpm. The new method developed is sensitive, reproducible, fast and easy to apply, improving the results from conventional LLE with very low solvent consumption, in line with the "Green Chemistry" requirements. In order to improve the extraction process with the different configurations of hollow fiber, a specially designed probe built with a 3D printer was used.

The method developed was applied for the simultaneous determination of DBPs in eight water distribution systems of Huelva area (southwest Spain) considering different resources.

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P-NDI-3

NEW PYROLYSIS-GC/MS SYSTEM INCORPORATED WITH ON-LINE MICRO-UV IRRADIATION FOR RAPID EVALUATION OF PHOTO, THERMAL, AND OXIDATIVE DEGRADATION OF POLYMERS: STUDIES ON EPDM AND HIPS

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Weather meter and outdoor exposure tests to study polymer degradation require a long period of testing time, e.g. for a few months. Volatile degradation products can't be analysed. A newly designed GC/MS-based technique [1] which employs a µ-furnace pyrolyzer combined with UV light from a Xenon lamp is used in two studies:EPDM and HIPS (containing BR).

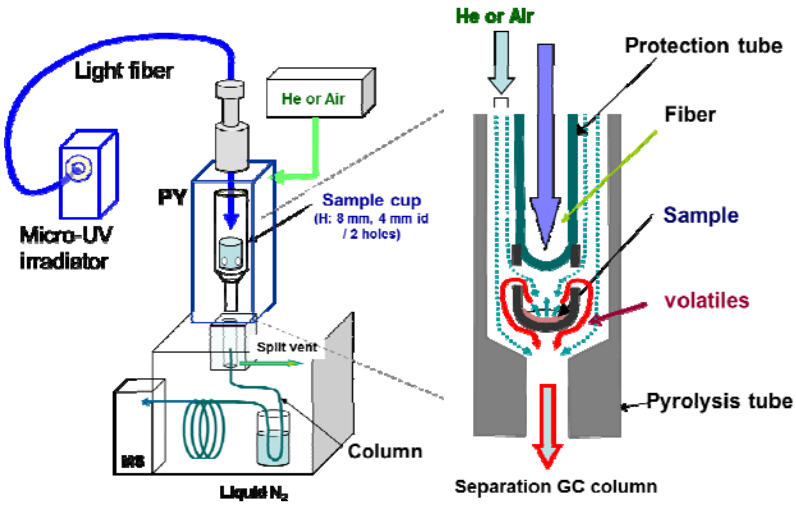

Fig 1: Schematic drawing of PY-GC/MS system incorporated with on-line Micro-UV (Xe) irradiator.

The evolved gas analysis of EPDM sample irradiated for 1 hr showed that the degradation by the peak intensity, peak top temperature, and half-height width of the main peak on the thermogram. Oxidized products originated from propylene units were formed as volatile degradation products. Straight chain aldehydes such as nonanol were observed. Formation of typical volatiles from the HIPS sample originating from PS and 2-propenal from BR, indicates the contribution of oxidative reactions in the polymer chains. The EGA thermogram of the residual HIPS sample is reflecting structural changes in HIPS during the irradiation. The micro irradiator achieved comparable degradation processes of polymeric materials 300x faster than conventional accelerated degradation test.

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P-NDI-4

SCREENING OF PHENOLIC COMPOUNDS IN OLIVE FRUITS AND LEAVES BY HPLC-ESI-MS^n

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Phenols are a major group of natural products that occur in all higher plants. Olive (*Olea europaea* L.) has been recognized as a source of biophenols that affect the organoleptic and nutraceutical properties of fruits and determine to some extend the biophenol composition in olive oil [1]. The main phenolic compound in olive fruits and leaves is oleuropein. However, the biophenolic composition in those tissues is often extremely complex and display a large diversity in structure and concentration [2, 3].

The integration of different analytical techniques as high-performance liquid chromatography (HPLC) with photodiode array detection (DAD) and electrospray ionization mass spectrometry (ESI-MS) provides universal detection that allows chemical screening of biophenols in a range of matrices and determination of molecular weight simultaneously [4].

In this work, a new methodological approach for screening of phenolic compounds of olive fruits and leaves was developed using HPLC-DAD-ESI-MS to clarify the complexity of the samples. On the one hand, HPLC coupled to electrospray time-of-flight mass spectrometry (HPLC-ESI-TOF-MS) provides excellent mass resolution, mass accuracy and isotopic pattern. On the other hand, HPLC coupled to electrospray ion trap multiple-stage tandem mass spectrometry (HPLC-ESI-IT-MS^n) is suitable for obtaining fragments ions of structural relevance for identifying target compounds.

The combined study of the data gives us the opportunity to know the fragmentation pathway of the main compounds and to distinguish between the different isomers of some phenolic compounds.

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P-NDI-5

CHIRAL SEPARATION OF NON-PROTEIN AMINO ACIDS BY ELECTROKINETIC CHROMATOGRAPHY. APPLICATION TO THE ANALYSIS OF FOOD SUPPLEMENTS.

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Non-protein amino acids can be present in foods as metabolic intermediates, as products formed during food processing or as additives to increase some nutritional and functional properties. They have also demonstrated to be relevant markers of the food quality and safety.

The L-forms of non-protein amino acids are present in nature. However, racemization into the D-forms may occur in foods due to the processing conditions or the action of microorganisms. In addition, they can even be present in supplemented foodstuffs due to the fraudulent addition of racemic mixtures. In fact, the use of D-enantiomers in the elaboration of foods and dietary supplements is forbidden by regulatory agencies [1].

The aim of this work was to develop new analytical methodologies based on the use of Electrokinetic Chromatography (EKC) enabling the enantiomeric separation of a group of non-protein amino acids of interest (pyroglutamic acid, norvaline, norleucine, 3,4-dihydroxy-phenylalanine, selenomethionine, 2-aminoadipic acid, citrulline, and pipecolic acid). The use of FMOC (9-fluorenylmethoxycarbonyl chloride) as derivatization reagent of non protein amino acids and their subsequent separation using formate buffer at acidic conditions (pH 2.0) and anionic cyclodextrins as chiral selectors allowed the enantiomeric discrimination of the non-protein amino acids studied. Changes in the enantiomeric migration order depending on the structure of the compound were observed. Moreover, the potential of the developed methodologies was demonstrated in the analysis of citrulline and its enantiomeric impurity in food supplements showing that D-citrulline was not detected in any of the supplements analyzed. The effects of the storage time on citrulline racemization were also investigated and no racemization process took place in those samples exposed to a long storage time.

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P-NDI-6

IMPLEMENTATION OF DIELECTRIC BARRIER DISCHARGE IONIZATION LC-MS SOURCE FOR FOOD, ENVIRONMENTAL AND BIOANALYTICAL APPLICATIONS

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The use of Liquid Chromatography-Mass Spectrometry (LC-MS) with electrospray ionization (ESI) is unarguably one of the most commonly employed techniques for trace analysis. However, there are certain groups of compounds which are not efficiently ionized by ESI, thus their determination requires the use of alternative or complementary ionization techniques such as atmospheric pressure chemical ionization (APCI). With the aim of extending the applicability of LC-MS coupling to a wider array of compounds with different physicochemical properties, new ionization sources have been developed. Recently, a Dielectric Barrier Discharge Ionization (DBDI) LC-MS source, which is based on the use of a low temperature helium plasma, was reported by Franzke and co-workers [1]. Because of the different species generated in the plasma jet as several mechanisms, including electron capture and proton transfer apply at the same time, DBDI source display the capability to generate ionizing species in both the positive and negative ionization modes covering an extensive range of polarity.

In this work, the performance of HPLC-DBDI-MS for trace determination in food, environment and bioanalytical applications has been examined, comprising a variety of multiclass compounds such as polybrominated diphenyl ethers (PBDE), pesticides, pharmaceuticals, lipids and phenolic compounds. The chromatographic eluent was provided by an Agilent 1290 Infinity HPLC equipped with a C18 column. This system was connected to a time-of flight mass spectrometer (Agilent 6220) equipped with a DBDI probe integrated in a commercial APCI-housing and configured in an axial position relative to the atmospheric pressure mass spectrometer inlet. LC-DBDI-MS performance for this application was assessed and compared with standard LC-MS sources (ESI and APCI). Further work is currently undertaken to optimize and improve preliminary results on the different applications envisaged for this approach.

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P-SP-1

NEW GENERATION BAμE DEVICES FOR THE DETERMINATION OF TRIAZINIC HERBICIDES AND METABOLITES IN ENVIRONMENTAL WATER MATRICES

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Triazinic compounds, such as simazine and atrazine, are among the most widely used herbicides, and are commonly used to remove broadleaf and grassy weeds in many crops. These herbicides and their metabolites have often been detected in atmosphere, water and soil, leading to many environmental problems. Nowadays, triazinic herbicides are considered dangerous contaminants that can cause harmful consequences to the human endocrine system. The inclusion of the degradation compounds is also highly important, since some of them are as toxic, or even more toxic as their parent compounds [1].
In the analytical point of view, the enrichment techniques commonly used to monitor these type of compounds are, in general, time consuming (*e.g.* solid-phase extraction) and many of them require considerable amounts of toxic solvents (*e.g.* liquid-liquid extraction), which makes these approaches neither convenient nor environmental friendly. Therefore, the application of new analytical strategies using adsorbent materials that can easily promote higher efficiencies, in particular to the more polar analytes, are definitely welcome in order to increase the recovery yields of pollutants, such as triazinic herbicides, at the trace level. Recently, bar adsorptive microextraction (BAμE) was proposed as a very effective sampling enrichment technique to monitor herbicides in water matrices.
The present contribution aims the application of new generation BAμE devices, as novel enrichment technology, to determine triazinic herbicides and metabolites in environmental water matrices. The discussion of the advantages and the effectiveness of this novel analytical tool is also addressed [2,3].

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P-SP-2

DETERMINATION OF ANTIDEPRESSIVE COMPOUNDS IN REAL MATRICES BY NEW GENERATION BAμE DEVICES

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Sample preparation is one of the most important task during trace analysis. For this reason, the modern sample preparation approaches aim the miniaturization of the analytical devices and easy manipulation, as well as small sample volumes and the reduction or absence of the usage of toxic organic solvents, in agreement with the green analytical chemistry principles [1].

Recently, bar adsorptive microextraction (BAμE) was introduced as a novel sample enrichment approach [2], using a bar shaped device simultaneously with a conventional Teflon magnetic stirring bar, at the bottom of a sampling flask. When the sample matrix is rapidly spinning around, due to the centripetal force promoted by the magnetic bar, the analytical device stays under free-floating motion just below the centre of the vortex ("floating sampling technology"). During a static process, the analytes migrate by diffusion from the sample bulk and then are retained in a convenient sorbent phase, where the microextraction takes place. Then the device is removed from the sample, transferred into a vial with an insert having the stripping solvent, where the desorption step takes place under sonication. The bar is then removed from the insert and, after encapsulation, the microextract become ready for instrumental analysis.

In this contribution, a new generation BAμE device is proposed, which is smaller and flexible in comparison to the original ones. For this particular device, the desorption process is similar to that described above, although it is not removed from the microextract prior instrumental analysis, enabling the straightforward manipulation involved during the back-extraction step. To assess the proposed improvements, several coating phases were tested, such as activated carbons and polymers and applied in the analysis of anti-depressive agents (bupropion, trazodone, citalopram and amitriptyline) on real matrices. The new generation BAμE devices showed much easier manipulation, low cost and requires even smaller volume (low μL level) of organic solvents during the back-extraction step, being a good alternative for the analysis of polar organic compounds in complex matrices.

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P-SP-3

A GUANIDINIUM IONIC LIQUID-BASED SURFACTANT AS EXTRACTANT SOLVENT IN AN *IN-SITU* DISPERSIVE LIQUID-LIQUID MICROEXTRACTION METHOD FOR DETERMINING ENDOCRINE DISRUPTING POLLUTANTS

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Ionic liquids (ILs) are non-molecular solvents with melting points below 100 ^{o}C. Among the unique properties of these new materials, it is interesting to highlight their high chemical and thermal stability, negligible vapor pressure at room temperature, and ease of synthesis. Moreover, the solubility, viscosity, and interactions of ILs with other compounds can be easily tuned by modifying their composition, which can lead to an impressive selectivity.

IL-based surfactants are a group of novel solvents that combine some of the inherit properties of ILs together with the possibility of forming micellar aggregates in aqueous solution, making them suitable in different extraction techniques. These ILs derivatives exhibit characteristics of cationic surfactants with lower critical micelle concentrations (CMC) than conventional surfactants with similar structures [1].

ILs and IL-based surfactants have been successfully employed as extractant solvents in dispersive liquid-liquid microextraction (DLLME) [2]. Since their first application, an increasing number of works have been reported, and different variations of this technique using ILs have been described. The *in-situ* DLLME mode is based on the utilization of a water-soluble IL as extractant solvent. This water-soluble IL is then transformed into a water-insoluble IL by a metathesis reaction using an anion-exchange agent. After centrifugation, a micro-droplet of the water-insoluble IL containing the preconcentrated analytes is obtained and can be sampled for further analysis. This approach avoids the use of an organic solvent as dispersive solvent.

Despite the success of imidazolium and pyridinium-based ILs in this microextraction technique, as an alternative to conventional halogenated solvents, recent works have pointed-out the toxicity of several ILs. In this sense, trends are focused on the design of more biodegradable ILs, based on morpholinium and guanidinium cations.

This work proposes an *in-situ* DLLME method using the environmental-friendly IL-based surfactant octylguanidinium chloride as extractant solvent, followed by high-performance liquid chromatography (HPLC) and diode array detection (DAD) for the determination of a group of personal care products and alkyphenols.

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P-SP-4

DETERMINATION OF PERFLUORINATED COMPOUNDS IN EDIBLE PLANT TISSUE BY LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY

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Treated wastewater and sewage sludge, generated during wastewater treatment, can provide agronomic benefits when applied onto soils. However, its increasing application onto agricultural lands can involve human health risks due to the presence, among others, of the so-called emerging pollutants. When agricultural lands are irrigated with wastewater or amended with sewage sludge, they can end up being accumulated on plant tissues [1].

In this work, we have focused our attention on perfluorinated compounds (PFC) because of their widespread distribution in treated wastewater and in sewage sludge, their toxicity, persistence and bioacumulation.

A sensitive and accurate analytical method for the determination of five perfluorinated carboxylic acids (from C4 to C8) and perfluorooctane sulfonate in plant tissue has been developed. The procedure involves sample pretreatment by lyophilization, ultrasound assisted extraction and clean-up of the extracts by dispersive solid phase extraction. Analytical determination was carried out by liquid chromatography–tandem mass spectrometry. Electrospray ionization in negative ionization mode was used. The most significant parameters affecting extraction and clean-up steps were optimized using Design of Experiments. Good linearity (R^2> 0.990), recoveries (between 77 and 94 %), precision (relative standard deviation values lower than 7 %) and limits of quantification lower than 0.025 ng g^{-1} dry weight were achieved. The method was satisfactorily applied to the determination of the target compounds in several vegetables.

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P-SP-5

OPTIMIZATION AND VALIDATION OF A METHODOLOGY TO QUANTIFY ENOLONES AND VANILLINES IN WINES BY AN AUTOMATED SOLID PHASE EXTRACTION FOLLOWED BY THEIR ANALYSIS THROUGH GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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This paper focuses on the analysis of two groups of molecules in wine, enolones and vanillines. Both types of molecules present a common characteristic, their great polarity. Sotolon, maltol, furaneol and homofuraneol belong to the first group. Their chemical structures present certain similarity among them, which leads to similar physicochemical and olfactory properties. This group of compounds is described with the terms “burnt sugar, candy sugar, caramel and maple”. Sotolon and furaneol are the most powerful aromatic molecules within them, being their odor thresholds estimated in water-ethanol matrix around 5 µg/L [1, 2]**.** The other group of molecules, vanillines, contributes to the oak related notes of alcoholic beverages.

This work presents an automatized strategy to quantify the following aromatic compounds in wine: maltol, furaneol, homofuraneol, sotolon, vanillin, methyl vanillate, ethyl vanillate and acetovanillone. The development of this strategy implied the use of Gilson system (GX-274 liquid handler). The proposed method is based on a solid phase extraction (SPE) using LiChrolut EN resins (50 mg). Three mL of wine were passed through a LiChrolut EN cartridge. After this, two consecutive washing up steps were applied. The first one consisted of 2mL of an aqueous solution at pH 8.0 containing 1 % of $NaHCO_3$. The second one was 2 mL of pentane containing 5 % (v/v) of dichloromethane. The elution of both kinds of compounds was carried out with 600 µL of dichloromethane with 5% (v/v) of methanol. The extract obtained was injected directly in a gas chromatograph with a quadrupole mass spectrometric detection system (GC-MS). The method showed good linearity in the range of occurrence for all compounds with a squared correlation coefficient higher than 0.9900, except for the ethyl vanillate that was lower. Matrix effects were not found. The detection limits obtained for all analyzed compounds were lower or equal to 0.7 µg/L. The precision was evaluated in reproducibility terms, obtaining in all cases DSR (%) below 12%. This methodology once optimized and validated was applied to quantify these compounds in a wide set of wines. As a result of these analyses, furaneol and vanillin exhibited odour aroma values, (OAV), higher than the unit in most of the samples.

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P-SP-6

DEVELOPMENT OF A MICROEXTRACTION METHOD USING A POLYMERIC SORBENT FOR TRACE ANALYSIS OF SELECTED PESTICIDES IN WATER SAMPLES

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Many pesticides used in agriculture are highly toxic both to the environment and to living organisms when their application is uncontrolled. Due to their highly persistent properties, pesticides bioaccumulate in food and can present a risk to animal and human health. Chlorpyrifos (CP) and diazinon (DZ) are two of the most widely used organophosphorus pesticides (OPPs), according to the United States Environmental Protection Agency (EPA). The European Water Framework Directive recognizes CP as a priority pollutant and has placed a limit of 0.1 μg L^{-1} as the maximum concentration permitted in fresh waters. Furthermore, a maximum level for individual pesticides of 0.1 μg L^{-1} has been established in water intended to be used for drinking purposes.
Gas chromatography with mass spectrometry (GC-MS) detection has been used as an analytical technique for pesticide monitoring. In many cases, an appropriate sample preparation step is necessary to simplify the matrix and to achieve the low regulated levels. Most common techniques used for this purpose are solid phase extraction (SPE), solid-phase microextraction (SPME) or liquid-liquid microextraction, among others. Here, a simple and effective method for the extraction and determination of three pesticides (chlorpyrifos, diazinon and cyprodinil) is developed using a polymeric sorbent prior to GC-ITMS. The polymeric sorbent is made of a polymer, cellulose triacetate (CTA), that provides the mechanical strength, and a plasticizer, nitrophenyl octyl ether (NPOE), that provides the material with elasticity and flexibility [1]. Analytes are extracted from water samples using a piece of the sorbent (3 cm^2), recovered with 1 mL of acetonitrile (ACN) and finally injected to GC-MS system. The main factors affecting the extraction efficiency are evaluated, including sorbent composition, stirring mode, extraction, and elution time. Under optimised experimental conditions, good linearity, limits of detection (0.2 μg L^{-1} for the three compounds), and recoveries of the analytes ranging from 69% up to 115% are achieved.

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P-SP-7

ANALYSIS OF MULTI-CLASS SYNTHETIC WATER-SOLUBLE DYES IN COSMETIC AND FOOD SAMPLES BY MATRIX SOLID-PHASE DISPERSION AND LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY

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Colour is one of the key factors in consumer products to make them attractive and hence, artificial dyes are widely used by manufacturers (medical, toy, plastic, food, and cosmetic industries). Most of synthetic dyes admitted as food additives in the EU Regulation (EC) Nº 1333/2008 are also employed in cosmetic formulations and their use is regulated by EU Regulation (EC) No 1223/2009.
Based on their chemical structure, dyes can be further divided in azo, triarylmethane, xanthene, indigo and quinoline classes; and they are usually used as the water-soluble sodium salts. Many of them contain one or more ionized sulfonic groups in their structure, which complicates the chromatographic separation by LC. In addition, due to the complexity of cosmetic and food samples, the development of extraction procedures to determine dyes in these matrices becomes a challenging task. A recent revision concerning the analysis in cosmetics evidences a lack of efficient methodologies in this field [1].

In this study, a multianalyte method based on reverse phase high performance liquid chromatography-electrospray ionization tandem mass spectrometry is developed for the simultaneous determination of 19 dyes, belonging to the five classes of synthetic water-soluble dyes, many of whom are employed both in cosmetics and in food samples. A satisfactory chromatographic separation and sensitivity is achieved using a low ionic strength mobile phase (only 3mM NH_4Ac). A miniaturized method based on matrix solid-phase dispersion (MSPD), applied successfully to the analysis of a few dyes in personal care products in a previous work [2], will be optimized in cosmetics and food matrices, such as candies. Parameters influencing the extraction efficiency, like dispersant, solvent and elution volume, will be evaluated by means of experimental design, employing only 0.1 g of sample. After chromatographic performance evaluation, the developed method will be validated in real samples and applied to the analysis of different commercial products.

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P-SP-8

MAGNETIC HYPERCROSSLINKED PARTICLES TO EXTRACT SWEETENERS FROM ENVIRONMENTAL SAMPLES

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Some studies have documented the occurrence of artificial sweeteners in the aquatic environment, becoming a new class of emerging organic contaminants (EOCs) in environmental water samples [1,2]. For these reasons, there is a need for accurate and reliable analytical methods to determine sweeteners in environmental samples. All these methods are based on liquid chromatography (LC) followed by mass spectrometry in tandem (MS/MS) as detector. However, one of most challenging parts of the analytical method concerns to the sample treatment, and so far, most of these analytical method also include solid-phase extraction (SPE) prior to the LC-MS/MS [2].

Recently, magnetic particles have been developed and are considered to be a promising material for different application such as water treatment [3]. A novel Q100 hypercrosslinked magnetic resin was developed and evaluated to this aim, with very successful retention results [3]. In viewing so, the aim of this study is to evaluate the retention behaviour of Q100 as material for extraction techniques.

This study presents the evaluation of the Q100 hypercrosslinked magnetic particles in the dispersive SPE (dSPE) mode followed by LC-MS/MS to determine a group of sweeteners from environmental water samples.

The different parameters affecting the extraction were firstly optimised in ultrapure water samples. Next, the optimised method was validated and applied to analyse different environmental samples such as river water, and effluent and influent sewage. The developed method successfully extracts the sweeteners and enables their quantification at lower ng/L levels in environmental samples.

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P-SP-9

A GREEN AND EFFECTIVE METHOD FOR THE EXTRACTION OF ACIDIC PPCPs IN SEDIMENTS AND OTHER SOLID MATRICES

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The assessment of environmental and human risk of emerging contaminants is not well-established [1] but, as a first step, their occurrence in environmental contaminants is being extensively studied. This work is aimed at developing and validating a method to determine acidic Pharmaceuticals of different therapeutic families (including illicit drugs) and Personal Care Product in sediment samples. The obtained results with this method will be compared with the QuEChERS extraction, which is the most common reported method for this purpose [2].

The developed method involves adding 5ml of McIlvaine-EDTA buffer, 5ml of Methanol and 5 ml of distilled water to 1g of lyophilized sediment or soil. This mix is sonicated and centrifuged. The supernatant is collected and added to 200ml of distilled water. Then, a Solid Phase Extraction (SPE) clean-up is carried out using Strata-X cartridges that are eluted with methanol. The extract are evaporated to dryness and reconstituted with 1ml of methanol–water (30:70, v/v). Ultra High-Performance Liquid Chromatograph (UHPLC) in tandem with a Triple Quad Mass Spectrometry (MS/MS) was used to determine the analytes after separation is carried out with a Kinetex column and a mobile phase consisting in 2.5mM NH4F in methanol and 2.5mM NH4F in water with 0.2ml min-1 of flow rate [3].

This new method provides higher sensitivity (limits of quantification (LOQs) 5-120 ng/L) and recovery (70-110 %) than QuEChERS (20-120 LOQs and 50-80 % recoveries) method for PPCPs. The method also provides good relative standard deviation (RSDs < 20 %). Some of the studied compounds were detected in low concentrations in sediments from the Turia and Jucar Rivers and L'Albufera Natural Park.

Acknowledgments
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P-SP-10

URINE AS SOURCE OF PROSTATE CANCER BIOMARKERS. EFFECT OF SAMPLE PREPARATION ON CAPILLARY ELECTROPHORESIS OF PROSTATE SPECIFIC ANTIGEN

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Population increase and ageing are accompanied by a raise in the incidence of prostate cancer (PCa). Early diagnosis before cancer spreading markedly increases chances of survival. To overcome the limited specificity of the current PCa marker (the concentration of prostate specific antigen (PSA) in serum) different approaches to find new prostate cancer markers are being explored. One of these approaches is to take advantage of the relationship between protein glycosylation and PCa [1]. Alterations in PSA glycosylation can be studied by capillary electrophoresis (CE). This technique makes possible to separate several isoforms (peaks) of PSA, each of them containing different molecular forms due to glycosylation or to other post-translational modifications (PTMs) of the glycoprotein [2].

Urine is an alternative source of biomarkers for PCa [3]. By using urine we are developing methods for studying alterations in PSA glycosylation and/or other PTMs related to PCa. To carry out these studies by CE, PSA must be isolated and concentrated previously from urine.

In this work the effect of the different steps involved in the purification of PSA from human urine has been studied. The results have been evaluated taking into account two critical factors: PSA recovery and compatibility with analysis of PSA isoforms by CE.

The effect on PSA recovery of several pre-treatment steps (centrifugation speed, filtration, concentration, etc) has been evaluated using enzyme-linked immunosorbent assays (ELISAs). After this pre-treatment, PSA was isolated from urine employing an in-house made immunochromatographic anti-PSA column. Some components of the urine matrix were eluted together with PSA, altering the CE profile of the glycoprotein. The use of an in-house made mouse IgG1 affinity column previously to the anti-PSA column made possible to obtain highly purified PSA, which allowed the CE-UV analysis of PSA isoforms from urine.

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P-FCH-1

PIPETTE-TIP EXTRACTION OF PROTEINS USING A POLYMER MONOLITHIC PHASE MODIFIED WITH GOLD NANOPARTICLES

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Solid-phase extraction (SPE) is currently one of the most widespread extraction techniques used for isolation/enrichment of low abundant analytes in a great variety of sample matrices. In particular, several SPE strategies have been accomplished for the enrichment of protein and peptides in protein analysis schemes and proteomics techniques. However, a limited choice of sorbents for protein species is available at present, consequently, the development of novel sorbent materials with satisfactory extraction efficiency and selectivity for protein species is highly desirable. Besides, the development of fast and comfortable extraction devices, such as pipette tips or other formats would reduce the required analysis time to isolate and preconcentrate these macromolecules in biological samples.

The use of porous monoliths as sorbents for sample preparation including pipette tip technology has recently been reviewed [1]. The key aspects of these monolithic SPE materials have relatively good binding capacity and low back pressure. The monolithic materials can be chemically bonded to the inner surface of the pipette tip providing a physically stable plug of the SPE sorbent. Moreover, the surface chemistry of the monolithic bed can be varied to achieve a desired selectivity. However, their use for enrichment of protein/peptides has been scarcely reported [2, 3].

In this work, a gold nanoparticle (AuNP)-modified monolith inside a pipette tip to isolate proteins was developed. The methacrylate-based monoliths prepared in 200 µL pipette tips were first modified with several ligands (ammonia, cysteamine and cystamine) to provide amino or thiol groups onto the pore surface of the material for the subsequent attachment of AuNPs. The sorbent with the highest coverage of AuNPs was selected to perform protein isolation studies. The analytical features of SPE sorbent (loading capacity and reusability) using bovine serum albumin (BSA) as probe protein were also established. The applicability of this sorbent was demonstrated by isolating BSA protein from cell cultures followed by SDS-PAGE analysis.

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P-FCH-2

APPLICATION OF A CHIRAL SEPARATION TO EVALUATE THE RACEMIZATION PROCESS OF ATROPINE IN *STRAMONIUM* SEEDS: INFLUENCE OF PH AND TEMPERATURE

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Jimson weed is a plant of the *Solanaceaes* family, gender *Daturae*, growing like weeds in cultivated fields and because of its toxicity and its impact on food and feed safety and animal food for humans is gaining interest. The main toxic components of this plant are scopolamine and atropine, which is a racemic mixture of (+) and (-)-hyoscyamine. Although atropine is a racemic mixture, only (-)-hyoscyamine, the enantiomer found naturally, is pharmacologically active, being a potent anticholinergic [1,2]. Racemization could occur in the process of extraction of (-)-hyoscyamine, if high and prolonged temperatures and basic pH are applied, but current studies are very limited [3]. Moreover, knowing the conditions under the racemization may occur is really interesting, since they are also applicable in cooking processes (cooking or baking) of food containing small amounts of seed plants belonging to the *Solanaceaes* family.

In this communication a study of the influence of pH and temperature in the process has been performed. For that, several studies have been performed at different pHs (3, 5, 7 and 9) and temperatures (30, 50 and 80 ºC). Furthermore, the racemization time was also evaluated at pH 5 and 9 at 80 ºC, observing that racemization is faster at higher pHs. To study these factors, an analytical method based on liquid chromatography coupled to high performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS) was used. In order to perform a suitable separation, a chiral column, Chiralpak-AY3, was used. The separation has been performed in isocratic mode using ethanol containing diethanolamine (0.1%) as mobile phase. Hyoscyamine extraction from *Stramoium* seeds was performed by a modified QuEChERS method.

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P-FCH-3

AMINES VERSUS IONIC LIQUIDS AS SILANOL BLOCKERS IN REVERSED-PHASE LIQUID CHROMATOGRAPHY

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In reversed-phase liquid chromatography using hydro-organic mobile phases, cationic basic compounds give rise to broad and asymmetrical peaks, as a result of the ionic interaction with the anionic free silanol groups present in the silica-based stationary phases (commonly derivatised with C18 groups). A simple way to improve the peak shape is the addition to the mobile phase of a reagent (an additive) with cationic character. This associates to the stationary phase to prevent the access of analytes to the free silanol groups. Cationic additives may interact electrostatically with the anionic silanols. The hydrophobic region of the additive may also be associated with the alkyl chains bound to the stationary phase, with the positive charge oriented towards the mobile phase. The access to the silanol groups is thus blocked, but in turn, the stationary phase is positively charged and will repel the protonated basic compounds, and unless their polarity is sufficiently low, will elute at very short times. In this work, a comparative study of the performance of a group of amines (butylamine, pentylamine, hexylamine, cyclopentylamine, cycloheptylamine, N,N-dimethyl-octylamine and tributylmethylammonium chloride), and the ionic liquids 1-butyl-3-methylimidazolium chloride and 1 hexyl-3-methylimidazolium chloride, as modifiers of the chromatographic behaviour of a group of basic compounds, is carried out. The study revealed that the performance of the cationic additives to block the silanol activity is explained by the additive size and its ability to be adsorbed onto the stationary phase.

P-FCH-4

CHARACTERIZATION AND CLASSIFICATION OF OLIVE OILS BY LIQUID CHROMATOGRAPHY-HIGH RESOLUTION MASS SPECTROMETRY AND CHEMOMETRICS

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The question of classification of vegetable and fruit oils has never been so up-to-date before. This is easy to substantiate by making a reference to the fact that during the last thirty years, there has been a growing interest in the use of olive oil worldwide. The increasing popularity of olive oils is mainly attributed to its high content of oleic acid, which may affect the plasma lipid/lipoprotein profiles, and its richness in phenolic compounds, which act as natural antioxidants and may contribute to the prevention of several chronic diseases such as cancer, diabetes and obesity. However, nowadays there are some concerns about labeled pure olive oil products that could be adulterated with oils coming from other oil of fruits or seeds such as sunflower, soy, and corn, or even extra virgin olive oil that can be adulterated with lower quality olive oils such as refined ones. Therefore, it is important to develop analytical methods for the correct authentication of vegetable oils.

This work was aimed at exploring suitable methods to characterize and classify vegetable oils according to the fruit/seed origin using liquid chromatography-high resolution mass spectrometry and chemometrics. For that purpose, 70 vegetable oils belonging to different origins were analyzed by UHPLC-MS/-HRMS (Q-Exactive) using a C18 reversed-phase column under gradient elution (acetonitrile:water and 0.1% formic acid). Full scan HRMS (*m/z* 100-1,500) at a resolution of 70,000 FWHM (full-width half-maximum) and data dependent MS/HRMS product ion scan at a resolution of 17,500 FWHM were used as the data subjected to principal component analysis (PCA) for sample classification. Employing an untargeted approach based on metabolomic fingerprints a good classification of samples regarding the type of fruit/seed was achieved after correcting and improving HRMS signal quality by using specific filters. Besides, on a targeted approach, polyphenolic signals were used for oil characterization. For that purpose, MS data was processed using ExactFinder v2.0 software, which allowed the interrogation of samples with a customized target database that contain a wide list of polyphenolic compounds. After further processing data by filtering signals with peak scores lower than 0.65, the most remarkable polyphenols for each oil type were identified and selected achieving a reliable classification of Spanish vegetable oils by PCA.

P-FCH-5

DISCRIMINATION OF BERRY-BASED NATURAL AND PHARMACEUTICAL PRODUCTS BY LC-HRMS UNTARGETED ANALYSIS AND PRINCIPAL COMPONENTS ANALYSIS

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Nowadays, the interest in healthy and natural dietary habits has increased, as it has been demonstrated that plant-derived foods can exert some beneficial effects on human health. That is in part the reason why the quality of food products has become an important concern for the consumers, based not only on organoleptic factors such as color, taste and aroma, but also on socioeconomic factors (e.g., geographical origin, processing and manufacturing processes). Polyphenols and low weight organic acid derivatives have proven to be adequate descriptors of some of these sample features, thus making polyphenolic data a powerful tool for the characterization of plant-based foods. Recently, American red cranberries and their derived products have shown health-promoting effects mainly related to their polyphenolic content (i.e., A-type proanthocyanidins). However, some of these products could be adulterated with more economic fruit extracts which do not contain the necessary bioactive polyphenols, making it necessary to develop analytical methods for the characterization, classification and authentication of fruit-based extracts according to their fruit of origin.

Therefore, in this work, more than 100 cranberry-, grape-, blueberry- and raspberry-based natural products as well as cranberry-based pharmaceutical products were extracted and analyzed by UHPLC-MS/HRMS, in both positive and negative ionization modes, with a Q-Exactive Orbitrap (Thermo Fisher Scientific) and an Ascentis Express (150x2.1 mm, 2.7 µm) C18 reversed-phase column using universal gradient elution conditions. Blank acetonitrile samples and a mixture of all the product samples were employed as quality controls. On an untargeted approach, full scan MS raw data were considered as metabolic fingerprints to be treated by principal components analysis (PCA). Chromatographic and MS data were processed to improve signal quality according to chromatographic peak width, and MS signal intensity and error. A good classification of the samples regarding the fruit of origin was obtained by PCA using negative ionization mode data. Moreover, nine polyphenol standards commonly found in the samples (i.e., proanthocyanidins and anthocyanidins) were characterized by MS/MS and MS/HRMS in order to elucidate their more common fragmentations for future sample characterizations.

P-FCH-6

CHARACTERIZATION OF FRUIT-BASED PHARMACEUTICALS AND NATURAL PRODUCTS BY LC-HRMS POLYPHENOLIC PROFILES AND PRINCIPAL COMPONENT ANALYSIS

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The quality of food products is an issue of great interest in our society. Consumer preferences regarding food products are often influenced by complex combinations of organoleptic (e.g. color, taste and aroma) and socioeconomic (e.g. ecological production, guaranteed origin and quality) factors. Several health-promoting properties of food products have partly been attributed to the presence of polyphenols. Apart from the sensory and functional attributes of polyphenols, their impact in the characterization, classification and authentication studies cannot be underestimated. Polyphenol contents seem to be related to food features such as geographical areas, variety and manufacturing practices. As a result, contents of polyphenols can be exploited as a source of analytical data to establish product classification. Today, fruit-based extracts are employed for the preparation of pharmaceuticals due to the beneficial health properties inherent to several polyphenols (i.e., polyphenols of American red cranberry help in the prevention of urinary tract infections). However, some of these products could be adulterated with more economic fruit extracts not containing the desired functional polyphenols. Therefore, it is important to develop methods for the correct classification of fruit-based pharmaceuticals and natural products.

In this work, a LC-HRMS method based on the determination of polyphenolic profiles and principal component analysis (PCA) has been proposed for the characterization and classification of fruit-based pharmaceuticals and natural products. A total of 57 polyphenolic compounds belonging to different families have been characterized by LC-HRMS and LC-MS/HRMS using an Orbitrap analyzer and an Ascentis Express C18 reversed-phase column under universal gradient elution conditions. Retention time, accurate mass errors, isotopic patterns and product ion scan spectra at a resolution of 17,500 FWHM (full-width at half maximum) have been used to build a customized target database of polyphenols. Then, more than 100 fruit-based natural products and cranberry-based pharmaceuticals have been analyzed with the proposed LC-HRMS method. HRMS data has been then processed by ExactFinder v2.0 software by using the customized target database list of polpyphenols, and the obtained polpyphenolic profiles subjected to PCA. A good classification of samples regarding the fruit of origin has been obtained, and the most discriminant polyphenols to each sample class, which could be proposed as future biomarkers, have been identified.

P-FCH-7

HPLC-UV CHROMATOGRAPHIC FINGERPRINTS AND PHENOLIC PROFILES FOR THE CHARACTERIZATION AND CLASSIFICATION OF OLIVE OILS AND OTHER VEGETABLE OILS

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Olive oil is a vegetable oil obtained by mechanical or direct pressing of the pulp of the olive fruit (*Olea europaea* L.). The olives, after being crushed to form a pomace, are homogenized and pressed. This oil is not subjected to any other treatment except for washing, decantation, centrifugation or filtration. The oil produced from this first press, known as extra-virgin olive oil (EVVO), is of the greatest qualitative olive oil containing the highest levels of beneficial constituents. Olive oils have become a very important factor in the Mediterranean providing beneficial health effects on the cardiovascular system because of their antioxidant capacity, mainly due to the presence of phenolic compounds. Recently, it has been suspected that some olive oil products could actually contain other vegetable oils of lower quality, produced from more economic fruits or seeds, or even refined olive oils. Hence, to protect consumers from possible frauds, the development of analytical methods to achieve classification and authentication of vegetable oils is necessary.

In this work, olive oils and other vegetable oils were analyzed and characterized by HPLC-UV. A chromatographic separation on a Zorbax Eclipse XDB-C8 reversed-phase column was proposed under gradient elution based on 0.1% formic acid aqueous solution and methanol for the determination of 14 polyphenols, allowing to obtain phenolic profiles in less than 20 min. Acceptable sensitivity (LOD values below 80 µg/L in the best of cases), linearity (r^2 higher than 0.986), and good run-to-run and day-to-day precisions (RSD values lower than 11.5%), and method trueness (relative errors lower than 6.8%) were obtained. The proposed HPLC-UV method was applied to the analysis of 72 vegetable oils (47 olive oils and 25 sunflower, soy or corn oils) after being treated with a simple liquid-liquid extraction method employing ethanol:water 70:30 (*v/v*) solution and defatting with hexane [1].

Polyphenolic profiles using peak areas and HPLC-UV chromatographic fingerprints were then analyzed by principal component analysis (PCA) to gain information on the most significant compounds contributing to characterization and classification of olive oils against other vegetable oils, as well as among Arbequina and Picual olive oil varieties. PCA results showed a noticeable separation among olive oils and the other classes. Besides, a reasonable discrimination of olive oils as a function of fruit varieties was also encountered.

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P-FCH-8

HPLC-UV CHROMATOGRAPHIC PROFILES FOR THE AUTHENTICATION AND IDENTIFICATION OF FRAUDS IN FRUIT-BASED EXTRACTS BY PARTIAL LEAST SQUARE REGRESSION

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Recently, there is an increasing interest in certain compounds that are present in foods and that are beneficial to human health. American red cranberry (*Vaccinium macrocarpon*) and its derived products have been recognized for its health-benefiting and medicinal properties associated to their high content on various types of polyphenols, mainly flavonoids such as anthocyanins, flavonols and flavan-3-ols. Flavan-3-ols include proanthocyanidins (PACs) and the most important bioactivity of A-type proanthocyanidins are their capacity to inhibit the adhesion of pathogenic bacteria to uroepithelial cells of the urinary tract, thus contributing to the prevention of urinary tract infections. However, nowadays there are some concerns on commercial red cranberry products sold in the market that could be adulterated with other more economic fruit extracts coming from grapes, blueberries or raspberries, which do not contain the adequate polyphenols to fight these infections. Therefore, it is important to develop analytical methods for the classification and authentication of fruit-based extracts according to their fruit of origin in order to prevent frauds to consumers [1].

In this work, high performance liquid chromatography with ultraviolet detection (HPLC-UV) was applied to the analysis and characterization of fruit-based extracts using a Kinetex C18 reversed-phase (100 mm x 4.6 mm i.d., 2.6 µm particle size) column under gradient elution with 0.1% (v/v) formic acid aqueous solution and methanol as the mobile phase. A simple extraction method, consisting of a sample sonication with acetone/water/hydrochloric acid (70:29.9:0.1 v/v/v) and centrifugation, was proposed. HPLC-UV chromatographic fingerprints were analyzed by principal component analysis (PCA) to extract information of the most significant profile data contributing to characterization and classification of analyzed samples according to their fruit of origin. Then, partial least squares (PLS) regression was employed to determine the percentages of grape-, blueberry, and raspberry-fruit adulteration in cranberry fruit extracts. The results showed that even mixture samples containing low percentages (2%) of adulteration could be distinguished from genuine cranberry extracts with prediction errors below 4%.

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P-FCH-9
GRAPHICAL-STATISTICAL ANALYSIS OF Py-GC/MS DATA OF SOIL ORGANIC MATTER IN FORECASTING MODELS FOR SOIL HYDROPHYSICAL PROPERTIES

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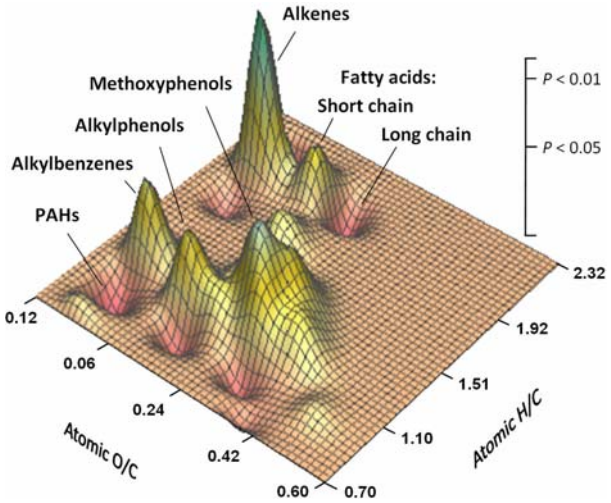
A lack of information exists on the relationships between the molecular composition of the soil organic matter (SOM) and soil quality indicators, in particular hydrophysical properties. This is especially relevant in Mediterranean environments where not only the low quantity of SOM, but mainly its quality is crucial to maintain minimum levels of resilience and functioning. In this study, molecular descriptors of humic acids (HA) were determined by analytical pyrolysis (Py-GC/MS) and studied for its possible correlations with soil physical properties *viz*, bulk density, porosity, aggregate stability, hydraulic conductivity (*b* and *c* Kostiakov parameters), permeability and water infiltration.

Significant chemometric models were obtained showing close relationships between the above physical descriptors and the total abundances of the 55 major pyrolysis compounds of the HAs in 12 soil samples from Central Spain [1]. The results were examined in *surface correlation plots* where different indices explaining the contribution by the individual pyrolytic compounds were shown as the 3rd dimension on the plane defined by its O/C and H/C ratios [2]. Due to scores for the different molecules tend to cluster in the plane according to its similar stoichiometry, the interpolated surfaces consisted of broad peaks—or compounds groups—indicating the distinct contribution by the structural domains of the HA macromolecules. The most perceptual graphics for effective visualization of SOM molecular constituents paralleling the soil physical properties were obtained with: i) the Pearson's linear correlation indices, as in the Figure, showing the SOM constituents associated with high aggregate stability as 3D peaks and the corresponding negative correlations as concave surfaces, ii) the 1+Pearson indices (positive values), iii) the coefficients of multiple linear regression models (MLR) after automatic backward variable selection (simplified surfaces in which non-significant molecular descriptors are not displayed) and iv) the variable importance for projection (VIPs) calculated from partial least squares regression (PLS) showing the principal structural relationships as positive 3D peaks surpassing a certain threshold.



Preliminary results of this exploratory approach indicate that pyrolitic yields of methoxyphenols (from plant lignins) and alkyl compounds from microbial biomass are correlated positively with porosity, permeability or aggregate stability, whereas hydraulic conductivity (*b* and *c* parameters) and water infiltration show a positive correlation with non-methoxylated aromatic compounds. The classical hypothesis of that highly aromatic and condensed SOM is associated with high soil quality, is not clear in our Mediterranean soils as regards physical quality, which behaves as a complex emergent property in close connection with structural surrogates for moderate hydrophobicity (alkyl domain in HAs) and low macromolecular aggregation (possible structural flexibility).

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P-FCH-10

INCREASED RESOLUTION OF COMPLEX MIXTURES OF DIURETICS USING A SERIAL COMBINATION OF C18 AND CYANO COLUMNS

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The separation capability of single HPLC columns is often insufficient to solve complex separations, due to the limited capability of single stationary phases to differentiate chemically similar solutes. A relatively simple solution is the connection in series of two or more columns (tandem columns), containing different stationary phases. Each combination behaves as a totally new column, and often outperforms the results given by the individual columns. The full exploitation of this approach requires, however, the development of powerful interpretive optimisation strategies, able to scan efficiently the capabilities of the separation system. The most powerful exploration strategies consider the column nature, length and order, and the profile of the gradient program, which should be preferably multi-linear. The number of candidate solutions to be examined is easily so high that the calculation cannot be carried out on a systematic basis, and natural computation methods are needed.

In this work, we explore the performance of tandem columns to increase the resolution of a complex mixture of diuretics. In previous work, we considered tandem systems combining up to five stationary phases. In this work, tandem columns are limited to only two nearly orthogonal stationary phases (in our case, C18 and cyano) to check whether such a simple tandem system still outperforms the capability of individual columns. Since the column nature was initially pre-selected, the optimisation was focused on the length of the coupled columns and the eluent composition (organic solvent content in isocratic elution and gradient profile of organic solvent in gradient elution). In all cases, both the resolution, calculated as peak purity, and the analysis time, were evaluated using Pareto plots.

A unique predictor system was developed in our laboratory, which implemented the different strategies with single and serially coupled columns, in both isocratic and gradient elution [1–3]. An interesting feature of the approach is that there is no need of additional experimental data: the same information used to characterise the single columns can be further applied to prospect the performance of gradients with serially-coupled columns. The mixture of diuretics was successfully resolved in practical times, in spite of the extremely poor performance obtained with the individual columns.

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P-FCH-11

FACTORS AFFECTING MATRIX EFFECT AND RECOVERY. CASE STUDY: MYCOTOXINS IN MILK.

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In the process of the LC-MS based analytical method validation, matrix effect and recovery are two important parameters to study. The change in the detector response of an analyte, caused by coeluting compounds, is known as matrix effect and it is probably the biggest drawback of the techniques based on LC-MS. There are not established permissible values for matrix effect and its total elimination is not needed, whenever reproducible; however, it is necessary to identify and quantify it [1]. Recovery is the amount of analyte not lost in an extraction process.

In a study on the presence of mycotoxins in cow's milk, slight variations (initial composition of the mobile phase and type of milk) have been introduced to analyze its impact on the matrix effect and recovery of mycotoxins. It has been found that the initial composition of the mobile phase (the same in which the sample was dissolved before chromatographic analysis) and the mobile phase gradient employed have a great impact on the matrix effect for DOM-1, HT-2 and T-2.

It has also been found differences in the matrix effect when applied the same methodology to whole and semi skimmed-evaporated milk. Although evaporated milk is reconstituted with water, the composition of the latter does not match to that of the whole milk, presenting in this last matrix a greater matrix effect for 11 out of 15 studied mycotoxins.

Finally, in terms of recovery, it has been found interesting behavior of fumonisins. Recovery values when analyzing whole milk are low compared with those obtained by applying the same method to semi-skimmed evaporated milk. Thus, the fat content and the process of milk manufacturing generate significant differences in these two matrixes.

Therefore, the aim of this work is to show the importance and need to validate methods employing the same studied matrix in the preparation of calibration samples, instead of supposing a matrix as representative of a food group.

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P-FCH-12

OPTIMAL MULTI-STEP GRADIENTS USING SINGLE AND TANDEM COLUMNS: CHROMATOGRAPHIC SEPARATION OF PROTEIC AMINO ACIDS DERIVATISED WITH *o*-PHTHALALDEHYDE AND N-ACETYL-L-CYSTEINE

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Along the years, a lot of effort has been invested in the development of reversed-phase liquid chromatographic (RPLC) methods to analyse amino acid compounds. Some reports deal with the RPLC separation of the *o*-phthalaldehyde/N-acetyl-L-cysteine (OPA/NAC) derivatives of the 19 primary proteic amino acids using gradient elution. These derivatives have given rise to sensitive procedures to analyse the amino acids using fluorescence detection. However, the amino acid derivatives are frequently resolved only in excessively long analysis times, even using gradient elution. When the analysis time is reduced, significant overlapping occurs for several compounds. Also, the columns available in the laboratory may not be capable of resolving the mixture of amino acids. In this case, the analyst can make use of the serial coupling of two or more columns with different stationary phases, which is equivalent to building a totally new column.

Multi-linear gradients often failed in the separation of the mixture of proteic amino acid derivatives at sufficiently short analysis times, owing to the trend of the four most retained amino acids to co-elute. In this work, we explore the possibilities of applying multi-isocratic gradients including steps with sudden reductions in the organic solvent content to resolve these amino acids and decrease the analysis time. In comparison with linearly sloped decreasing gradients, multi-isocratic gradients have the advantage of not contributing to the peak broadening, as well as giving rise to the quick restoration of the baseline after performing the organic solvent change. A third advantage is the possibility of applying algebraic integration when the retention model allows it.

The approach was applied to the separation of OPA/NAC derivatives using a 25 cm long Inertsil ODS-3 C18 column (Análisis Vínicos, Tomelloso, Spain) and a hybrid column built by coupling 7.5 cm long ACE Technologies (Aberdeen, Scotland, United Kingdom) pentafluorophenyl and C4 columns. In both cases, the mixture of amino acid derivatives was successfully resolved in practical times.

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P-IA-1

H-C-O ISOTOPE RATIO ANALYSIS AS A VALID TOOL TO CERTIFY THE AUTHENTICITY AND GEOGRAPHICAL ORIGIN OF WINE VINEGARS WITH PROTECTED DESIGNATION OF ORIGIN

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Wine vinegar is the most commonly used vinegar in Mediterranean countries and Central Europe. This product is the result of the conversion of must sugars into ethanol by the action of yeasts, and the subsequent ethanol oxidation by acetic acid bacteria [1]. Andalusia is a Spanish region traditionally associated to wine culture where three categories of wine vinegars have been protected with a legal framework called Protected Designation of Origin (PDO) due to their unique characteristics. These three PDO vinegars are “Vinagre de Jerez” (also known as “Sherry wine vinegar”), “Vinagre Condado de Huelva” and “Vinagre Montilla-Moriles”.

These vinegars have high prices in the market due to their high quality, the long aging time and the high cost of their production. That explains the fact that these products are vulnerable to fraud [2] and new tools are required to fight against falsification or mislabeling. Frauds increase in these high quality vinegars creates needs for better systems to determine their quality, authenticity and geographical origin. In this context, the analysis of stable isotope ratios of hydrogen (D/H), carbon ($^{13}C/^{12}C$) and oxygen ($^{18}O/^{16}O$) has already been introduced as an officially accepted method in food authenticity and origin determination [3].

The aim of this study was to determine the hydrogen, carbon and oxygen isotopic composition of a selection of wine vinegars samples belonging to the three aforementioned Andalusian PDO wine vinegars to assess the utility of this technique as a guarantee of their authenticity and geographical origin. Data obtained by this technique were compared with the results obtained in previous analyzes, such as the determination of mineral content and/or spectroscopic data.

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P-IA-2

NATURAL ADDITIVES IN ACTIVE FOOD PACKAGES. PYROLYSIS COMPOUND SPECIFIC ISOTOPE ANALYSIS (Py-CSIA)

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Isotope ratio mass spectrometry (IRMS) has become a key tool for scientists in many disciplines and the practical applications of the technique are continuously growing. While no or little sample preparation is required for bulk isotopic analyses, for compound-specific isotope analysis (CSIA) usually intermediate preparative procedures are required prior to chromatographic analysis to isolate analytes from geological, biological or synthetic materials. In addition, non-volatile compounds must be made amenable to GC by derivatization or treated before chromatographic separation adding complication. Analytical pyrolysis is a long established technique that can help overcome preparative manipulation of samples. The sample is heated up in an inert atmosphere (usually He) to decompose into smaller units (pyrolysate) which are transferred for chromatographic separation to a GC connected to an appropriate detector.

In this communication we describe the results obtained by hyphenating analytical pyrolysis (Py-GC) with carbon IRMS for the analysis of a polylactic acid (PLA) based film extruded with variable quantities of natural plant extracts or essential oils for use in active food packaging.

Chemical structural information of pyrolysates was first determined by conventional analytical pyrolysis (Py-GC/MS). Bulk $\delta^{13}C$ measures were performed for each material by EA-IRMS. The direct study of $\delta^{13}C$ carbon isotopic signature in specific compounds was done by coupling a pyrolysis unit to a gas chromatograph connected (via Thermo Scientific GC-Isolink System) to a continuous flow IRMS unit (Py-GC-(FID)-EA-IRMS). Using this Py-CSIA device it was possible to trace natural additives with light $\delta^{13}C$ signatures derived from C3 photosystem vegetation, from the heavier bio-plastic backbone usually derived from corn (C4 vegetation) starch. Finally the results are discussed in terms of the potential of this new chromatographic application for food traceability and security.

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P-IA-3

DETERMINATION OF FOUR ENDOGENOUS ANABOLIC ANDROGENIC STEROIDS IN URINE BY UHPLC-MS/MS AND ISOTOPE PATTERN DECONVOLUTION

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In this work we present an analytical method for the determination of testosterone (T), epitestosterone(EpiT), androsterone (AN) and etiocholanolone (Etio) in urine using an isotope dilution quantification approach, which allows the simultaneous analysis of the analytes in a single injection without needing methodological calibration [1].

10 human urine samples were collected from healthy volunteers in order to perform the initial analysis and method development. Sample treatment was performed following the general guidelines from the World Anti-Doping Agency (WADA) [2]. Hydrolysis of the glucuronide conjugates was performed by enzymatic reaction with β-glucuronidase *E. coli*, followed by a liquid-liquid extraction with methyl tert-butyl ether and analysis on an ultra-high pressure liquid chromatography – tandem mass spectrometry system (UHPLC-MS/MS). Quantification was successfully accomplished by isotope pattern deconvolution (IPD) using deuterated analogs of the compounds of interest (d_3-T, d_3-EpiT, d_4-AN and d_5-Etio) without isotopic effects.

The present method was validated with two certified reference materials (CRM), which consisted of freeze-dried urine samples with certified concentrations of several steroids (MX002 and MX005 from NMI Australia). Within-day repeatability (n=5) and inter-day reproducibility (n=4) were assessed by analyzing aliquots of the reconstituted CRMs. Repeatability experiment provided relative standard deviations (RSDs) between 1.4% and 4.5% for all analytes and CRMs, while the reproducibility experiments resulted in RSDs between 1.8% and 9%. The accuracy of the method was evaluated as the recovery percentage comparing the mean of the results obtained in all experiments versus the certified values. The results obtained for MX002 and MX005 materials fell between 86%-104% and 82%-103% of recovery, respectively.

The present work showed the potential of applicability of isotope dilution-based methodologies such as IPD in the field of anti-doping control, especially for steroid profiling. This method provided a reliable, accurate and fast determination of the most important EAAS concentrations currently detectable in LC and used to calculate the main biomarkers (T/EpiT, AN/Etio and T/AN ratios) included in biological passport's steroidal profile [3].

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P-IA-4

EVALUATION OF UNCERTAINTY SOURCES IN THE DETERMINATION OF TESTOSTERONE IN URINE BY CALIBRATION-BASED AND ISOTOPE DILUTION QUANTIFICATION METHODS USING UHPLC-MS/MS

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In this work we present the evaluation of the different sources that contribute to the total uncertainty in the measurement of the concentration of testosterone in human urine. Total uncertainties and individual contributions where evaluated for 3 different quantification methods: calibration with internal standard, standard additions and isotope dilution using isotope pattern deconvolution (IPD).

In order to obtain samples along the normal testosterone concentration range, that is between a few ng/mL to 100 ng/mL [1], 6 synthetic urines where prepared by mixing 12 individual samples in pairs. The 6 samples were firstly analyzed by standard additions method to determine the reference value. 5 replicates in different weeks were analyzed by calibration with internal standard and IPD methods. The sample treatment applied in all three methodologies was in accordance to the World Anti-Doping Agency (WADA) guidelines [2]. Liberation and extraction of testosterone was accomplished by hydrolysis of the glucuronide conjugate by means of enzymatic reaction with β-glucuronidase *E. coli* followed by liquid-liquid extraction with methyl tert-butyl ether. Uncertainty was evaluated using the Kragten calculation method, which is based on the general formula of error propagation [3].

The determination by standard additions (n=1) provided relative standard deviations (RSD) between 2.2% and 4% and they were produced, in variable amounts, mainly by the instrumental measurement itself plus the uncertainty of the volume of sample taken (between 52% and 90% of the total uncertainty). Calibration with internal standard quantification provided RSDs (n=5) between 0.6% and 4.2% which were produced mostly by the instrumental measurement (73%-79%). On the other hand, IPD method resulted in RSDs between 1.1% and 2.7% (n=5), with an instrumental contribution of 33%-90%. The remaining uncertainty came from the addition by volume of the isotope-labelled testosterone standard needed for this methodology (7%-45%), which could be further reduced if performed by weight.

This work showed the margin of improvement of the uncertainty and dispersion of the results in complex matrices such as biological fluids for 3 different analytical approaches, highlighting the potential of isotope dilution determinations in steroid profiling.

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P-OA-1

SEARCHING POTENTIALLY ALLERGEN SUBSTANCES (PAS) IN EAU DE COLOGNE USING ANALYTICAL PYROLYSIS (Py-GC/MS) AT SUB-PYROLYSIS TEMPERATURE

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The International Fragance Associaton (IFRA) following the EU Cosmetic Directive has developed GC-MS analytical method for the determination of 24 volatile chemicals that are ingredients in finished cosmetics and personal care products. These compounds are potentially allergen substances (PAS) that have been suspected to elicit skin sensitization. Their presence must be indicated in the list of ingredients when their concentrations exceed 0.01% for rinse-off products and 0.001% for leave on products.

Several analytical methods have been developed for the determination of fragrance allergens in different samples by GC-MS and/or GC-MS/MS [1, 2, 3]. The aim of this study is to explore the possibility of analyze simultaneously the 24 PAS using analytical pyrolysis (Py-GC/MS). The analyses were performed in a double-shot pyrolyzer (Frontier Lab 2020i) attached to a GC/MS system (Agilent 6890N + 5973MSD). Detailed chromatographic conditions can be found elsewhere [4]. Fragrance aliquots (0.1 µL) were poured on ultra clean quartz wool into a small stainless steel crucible (Eco-cup SF) and dropped in a preheated micro-furnace at sub-pyrolysis temperature of 200 °C for 1 min before the evolved gases were transferred to the GC/MS for analysis. Compounds assignment was via single-ion monitoring and by comparison with published and stored (NIST and Wiley libraries) data.

Up to 50 different compounds could be directly identified in three different commercial eau de cologne samples. These included known synthetic and natural common ingredients in such light, fresh and fruity fragrances (Musk, Musk T, Cashmeran, Dihydromyrcenol, PEA, OTBCH, Ambrox, Citronellol, Hedione, Vanillin, Lilial, Helional,…) other components like possible sun screens (Parsol) or pheromone compounds (Hexadecadienols), waxes (*n*-alkane series C_{24}-C_{35} max C_{29}) and contaminants (DEP, Phthalates) were also detected. In addition 9 compounds found were PAS among those included in the “26 allergens rule” list: Bencyl salicylate, Coumarin, Geraniol, Lilial, Linalool, Benzyl benzoate, Hexyl cinnamaldehyde, D-Limonene and α-Isomethylionone.

These results, although provisional, opens a promising application of analytical pyrolysis as a rapid fingerprinting tool and for the rapid screening for PAS components in fragrances and cosmetics.

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P-OA-2

ANALYTICAL PYROLYSIS OF ACID PRECIPITABLE POLYMERIC LIGNIN (APPL) FROM THE SOLID-STATE FERMENTATION OF WHEAT BIOMASS WITH *Streptomyces ipomoeae*

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Streptomycetes produce enzymes able to depolymerize lignin in solid-state fermentation (SFF) conditions and therefore are of interest for biopulping purposes. In recent studies a thermostable laccase (SilA) produced by *Streptomyces ipomoeae* CECT 3341 presenting both physico-chemical and structural characteristics usually uncommon among microbial laccases was isolated that opened up the biotechnological interest of this enzyme *i.e*. high resistance to alkaline conditions and to high concentrations of sodium chloride [1]. For this study, the wild strain (SilA) and a laccase-negative mutant (SilA−) obtained through gene disruption were grown on wheat straw as substrate under SSF conditions. In addition, a non-inoculated substrate was used as control. After 7 days of incubation the APPL extracted with water were quantified and studied by Py-GC/MS at moderate temperature (350 °C).

The APPL yield was 12 times and 6 times higher for the wild-type strain (SilA) than for the control and mutant strain (SilA−), respectively. Under the chromatographic conditions used [*i.e.* 2], the chromatograms could be divided in three parts where main biogenic compounds elute; a first part (min 2-5) dominated by polysaccharide-derived compounds, from min 5-14 lignin-derived compounds and from min 14 to the end of the chromatogram lipid compounds including fatty acids (FA14, 16 & 18), long chain alkanes (C27-C33) and sterols. Polysaccharides were the main pyrolysis compounds detected in the control (89.0 %) and SilA− mutant strain (60.9 %) APPLs, being a minor component in the SilA strain (5.4 %) that was dominated by lignin derived compounds (77.3 %). The pyrolysates from the wild SilA and SilA− strains present a similar distribution of lignin subunits (H, G, S) and an equivalent degree of oxidation. In control APPL there was an absence of H and dominance of G type subunits and higher relative abundance of non-oxidized alkyl phenols. However, a shortening of lignin propyl side chains and a higher relative abundance of oxidized moieties (ketones and acids) where the predominant features of SilA and SilA− APPLs. This result indicates the occurrence of oxidative Cα-Cβ cleavage of propyl side chains in lignin by both strains.

In conclusion, *S. ipomoeae* has high lignin solubilizing activity in SSF conditions. Although laccase is the main enzyme involved, other oxidative enzymes are likely to contribute. The behaviour of the laccase-negative mutant (SilA−) could indicate the presence of alternative oxidative enzymes which affects/modify the lignin in a similar manner than laccase but with lower efficiency.

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P-OA-3

OPEN COLUMN LIQUID CHROMATOGRAPHY AND THIN LAYER CHROMATOGRAPHY FOR SARA ANALISYS OF CRUDE OILS

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Liquid Chromatography (LC) and Thin Layer Chromatography coupled to a Flame Ionization Detector (TLC-FID) are two chromatographic techniques widely used in oil industry for bulk crude oil and bitumen characterization. Both techniques allow to separate compounds into classes to perform the so-called SARA analysis (Saturates, Aromatics, Resins and Asphaltenes). The relative abundance of these four fractions helps to assess oil quality, detect tar mats, and is useful to predict potential flow assurance problems and to establish oil-oil and oil-source rock correlations.

TLC-FID (Iatroscan- IP 469) has long been used as a rapid and inexpensive way to determine SARA fractions [1]. Very small amounts of sample are needed and no previous asphaltene separation is required. However, polar fraction determination has been reported to be biased by variable FID response factors sensitive to the heteroatom content [2]. Additionally, heavy oils and tar sands rich in polar compounds are affected by separation and quantitation problems [3]. Although considerably more time-consuming, LC serves as an alternative method and at the same time as a preparative technique for other geochemical analyses (biomarkers, stable isotopes, ...). Faster, more reproducible, and more readily automated HPLC methods have now displaced clay-gel adsorption chromatography (ASTM D2007) and have been in-house adapted and improved to achieve clean quantitative separations [4].

In this work we have used a simplified open-column LC methodology with silica gel/alumina-packed serological pipettes for gravimetric SARA fractionations. Four oils with different physico-chemical properties were selected: a light oil from Abu Dhabi, a medium gravity oil from Colombia and two heavy and highly paraffinic oils from Thailand. The oil samples were initially topped to 250ºC for volatile quantitation. After asphaltene precipitation the maltene fraction was charged into the column. The gravimetric values obtained with this technique have been compared with those determined by TLC-FID from peak areas.

Although results are rather consistent, some differences are detected. For example, we systematically observed that the % of aromatics was higher by TLC-FID compared to our open-column LC method. LC losses can be attributed to the resin fraction due to incomplete elution of the strongly retained polar fraction. We conclude that both techniques can be used complementarily, however, it is important to use the same analysis method when comparing SARA results. Further work will be done to share more light on these results.

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P-OA-4

URINARY METABOLITES OF DI-*iso*-NONYLPHTHALATE (DiNP). DETERMINATION BY UHPLC-QqQ-MS^{2}AND HUMAN EXPOSURE ASSESSMENT

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Di-*iso*-nonylphthalate *(*DiNP) has replaced di(2-ethylhexyl)phthalate (DEHP) as the major plasticizer of polyvinylchloride (PVC) polymers because the later has been regulated and its use has been limited in several applications. Because of that, DiNP production is expected to increase at the expense of DEHP in the next few years. Non-PVC uses of DiNP include rubbers, inks, paints, lacquers, adhesives, and sealants. For these reasons, the determination of human DiNP exposure is of utmost importance nowadays. The analysis of exposure to commercial DiNP is especially challenging compared to other phthalates because technical DiNPs are compose of a complex mixture of branched-chain dialkyl phthalate isomers, predominantly containing nine carbons in the alkyl chain. Presently, there are two different DiNP types being used (CAS 68515-48-0 and CAS 28553-12-0). These DiNP mixtures have many of their constituents in common, and differ in their isomeric composition. Therefore, the metabolites of DiNP present in urine would also be an isomeric mixture [1].

For the general population, oral exposure has been considered the major route, including inhalation of air (indoors and outdoors), ingestion of food, incidental ingestion of soil, and ingestion of dust (indoors), as well as direct contact with products containing phthalates [2]. Generally, phthalates are metabolized and excreted quickly and do not accumulate in the body. Ingested phthalate diesters are initially hydrolyzed in the intestine to their corresponding monoester, which is then absorbed, and could be further oxidized in the body. Hydrolyzed monoesters and oxidation products can be glucuronidated and predominantly excreted via urine [3].

Biological monitoring of internal DiNP exposure through oxidized metabolites is especially eligible because it is not influenced by external DiNP contamination and because it measures each individual's DiNP burden over all routes of exposure. The simple monoester mono-*iso*-nonylphthalate (MiNP), which has been used in some studies, seems no to be a good indicator for DiNP exposure because it is extensively further oxidized by ω and β-oxidation before renal excretion [4].

We present here how the analyses of isomer mixtures of three metabolites of DiNP, one primary metabolite (mono-*iso*-nonyl phthalate; MiNP), and two secondary metabolites (mono-(4-methyl-7-hidroxy octyl) phthalate; 7-OH-MMeOP) and mono-(2-methyl-6-carboxi heptyl) phthalate; 6-cx-MMeHP) in urine samples have been addressed. The developed methodology was further applied for estimating the human exposure to DiNP.

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P-OA-5

ASSESSMENT OF PESTICIDE RESIDUE EXTRACTION IN HONEY AND HONEYBEES

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Honeybees play a crucial role in wildlife, and in agrarian lands carry out most of the pollination. Nectar collection from crops and beekeeping practices expose honeybees to many pesticides, which can contaminate honey during its production [1]. The development of efficient pesticide extraction procedures for honey and honeybees in an economic way and following the last recommendations within green chemistry is required [2].

Three extraction procedures were compared in terms of sensitivity, accuracy, precision, time, cost and versatility. Solid Phase Extraction technique and solvent-based approach were the pesticide extraction procedures for honey and honeybees, respectively. The QuEChERS protocol was used for both matrices. Honey is a highly sugar concentrated solution (mostly fructose). From an analytical point of view, after water dilution, honey can be extracted using protocols similar to those applied to water. On the contrary, honeybees are rich in proteins and lipids and need more sophisticated and extensive sample-preparation methods.

The sensitivity of the methods was estimated by establishing the limits of quantification (LOQs), which were from 0.2 to 10 $ng \cdot g^{-1}$ and from 0.3 to 10 $ng \cdot g^{-1}$ for honey and honeybee matrices, respectively. Solvent and SPE methods were slightly more sensitive than QuEChERS approach. Matrix effects were mostly suppressive in both matrices and ranged from -60 to 50 and from -60 to 35% in honey and honeybee matrices, respectively. Recovery values (as accuracy) were from 34 to 96% for honeybees, whereas precision (as RSDs) were in all cases <20%. Honey matrix showed recoveries that ranged from 30 to 96%, and RSDs were <20% except for 17 compounds that were from 21 to 42%. SPE and solvent-based extraction procedures showed equivalent accuracy and precision values to QuEChERS. The sensitivity, accuracy and precision results, together with versatility, quickness and low cost make QuEChERS the most efficient protocol for the extraction of pesticides in honey and honey bee matrices.

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P-OA-6

DETERMINATION OF NEONICOTINOIDS IN URINE BY LIQUID CHROMATOGRAPHY COUPLED TO ORBITRAP HIGH RESOLUTION MASS SPECTROMETRY

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Neonicotinoids are a class of neuro-active insecticides chemically related to nicotine. These compounds are the first new class of insecticides introduced in the last 50 years [1]. Neonicotinoid pesticides are systemic insecticides that possess nicotinic acetylcholine receptor (nAChR) agonist activity. Although neonicotinoid pesticides can be environmental neurotoxicants, they are widely used to protect vegetables, rice, and fruit trees because they are effective to control a wide range of pests [2]. Because most neonicotinoids can be bound to insect neuron receptors much more strongly than to mammal neuron receptors, these insecticides are selectively more toxic to insects than mammals.

For the determination of these compounds, liquid chromatography (LC) coupled with low resolution mass spectrometry is commonly used. However, the high resolution Exactive-Orbitrap mass analyzer offers multiple advantages because its high sensitivity and its ability to analyze an unlimited number of compounds by means of accurate mass measurements combined with high resolving power [3]. This mass spectrometry analyzer operates in the full scan mode and provides accurate mass measurements (<5 ppm), allowing selective detection of residues at low concentration levels in complex samples, such as urine. The use of semiautomated techniques for sample preparation, such as turbulent flow chromatography (TFC) or solid phase extraction (SPE), can be considered to increase sample throughput. TFC consists of a sample preparation system based on a column with large and porous stationary particles combined with a high flow rate of mobile phase. TFC and SPE provide online samples extraction and cleanup, allowing the reduction of the overall analysis time compared to traditional off-line methods [4].

In this study, a method has been developed for determining 7 neonicotinoid (acetamiprid, imidacloprid, clothianidin, dinotefuran, nitenpyram, thiacloprid and thiamethoxam) in urine by liquid chromatography (LC)-Exactive-Orbitrap analyzer. The samples were extracted evaluating two different fast on-line systems: turbulent flow (TurboFlow) and SPE, comparing several parameters as sensitivity, sample throughput and repeatability.

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P-OA-7

IDENTIFICATION OF A DERIVATED COMPOUND OF FLONICAMID USING AN ORTHOGONAL APPROACH BY HIGH RESOLUTION MASS SPECTROMETRY AND NUCLEAR MAGNETIC RESONANCE

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Advances in analytical techniques with high sensitivity allow the detection of a growing number of compounds at low concentrations. This has been favored by the increased availability of high resolution mass spectrometry (HRMS) analyzers, as time of flight (TOF) or Orbitrap. These analyzers have several important features for the detection and identification of compounds, and target and non-target analysis modes can be performed. However, unequivocal identification of compounds by HRMS is achieved only when standards are available [1]. Otherwise it is necessary to confirm them by a complementary or orthogonal technique, being nuclear magnetic resonance (NMR) spectroscopy the most widely used [2] for definitive compound identification. The main weakness of NMR is its lack of sensitivity compared with HRMS, although it is probably the most selective analytical technique available in order to provide unambiguous structure characterization of a certain molecule. In consequence, the combined use of LC-HRMS and NMR is a powerful strategy towards comprehensive route fragmentations.

Flonicamid (N-(cianomethyl)-4-(trifluoromethyl)nicotinic acid) is a systemic insecticide, and it can be degraded in several metabolites under standard conditions [3], and the main are 4-(Trifluoromethyl)nicotinol glycine (TFNG), 4-trifluoromethylnicotinic acid (TFNA) and 4-trifluoromethilnicotinamide (TFNA-AM). For this reason a study of the behavior of flonicamid in acidic (similar to the acidity of the orange), neutral and basic conditions was evaluated by HRMS and NMR. Also the effect of temperature at different pHs was studied to check whether the effect of heat can promote degradation of this compound.

Results show that a new compound was identified. It was a deuterated compound of flonicamid and its occurs when flonicamid was treated with deuterated water at basic pH and high temperature. Therefore, this compound was really interesting to further chemical or biochemical processes involved in flonicamid degradation studies, due to some reactions could be studied monitoring this deuterated compound.

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P-OA-8

A NOVEL BENCHTOP GC-TOFMS FOR FAST TARGETED ALLERGEN SCREENING AND NON-TARGETED CHARACTERIZATION FOR PERSONAL CARE PRODUCTS

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Some fragrance compounds in personal care products are allergens or skin irritants, so it is important to be aware of their presence in a product. Manufacturers must provide this information for compliance with rules, such as the European Cosmetics Directive that regulates 26 contact allergens. GC-TOFMS is well-suited for this targeted screening and also for non-targeted characterization. A GC-TOFMS method was developed to complete the analysis in approximately 5 minutes. Chromatographic resolution along with mathematical deconvolution of the TOFMS data separated the target allergens within the standards. Calibration equations were compiled from 1 ppb to 1 ppm levels (on-column) with excellent linearity and correlation coefficients. The calibrations were applied to various commercially-available perfume and cologne samples and quantitative information for the targeted allergens was determined. In addition to the target allergens, these data also provide excellent unknown characterization information for non-targeted analytes from the same injection. TOFMS provides simultaneous non-targeted analyses because of the full-mass range data acquisition. Thus, additional non-targeted characterization and comparison of the perfume samples were also performed. Numerous similarities and differences between the samples are highlighted for an improved understanding of the aroma profile of these products. The reported method reduces analysis time for allergens screening and increases acquired characterization information for PCPs.

P-OA-9

ANALYSIS OF MONOAMINE OXIDASE (MAO) ENZYMATIC ACTIVITY BY HPLC COMBINED WITH A SPECTROPHOTOMETRIC ASSAY AFTER OXIDATION WITH A PEROXIDASE

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Monoamine oxidase (MAO) is a flavin adenosine dinucleotide (FAD)-containing enzyme located at the outer membranes of mitochondria that catalyses the oxidative deamination of neurotransmitters and xenobiotic amines. It appears as two isozymes, MAO-A and -B, distinguished by differences in substrate and inhibitor selectivities [1]. The oxidation of amines by MAO results in the production of hydrogen peroxide and aldehydes which represent a risk factor for oxidative injury [1,2]. MAO inhibitors are useful as antidepressants and neuroprotectants [1]. In this work, a RP-HPLC method is used to determine the activity and inhibition of MAO [3, 4], and the method is combined with an assay based on the oxidation with a peroxidase. The method is applied to study the inhibition properties of bioactive compounds such as β-carboline alkaloids and flavonoids present in foods and plants [5,6].

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P-OA-10

EVALUATION OF THE INTESTINAL TRANSPORT OF MAIN PHENOLIC COMPOUNDS FROM ROSEMARY EXTRACT ACROSS CACO-2 CELL MONOLAYER BY UHPLC-TOF MS

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Rosemary is a well-known edible herb from the Lamiaceae mint family with a variety of properties, such as, antioxidant, anti-inflammatory, chemoprotective, antiadipogenic, and antiproliferative activities [1]. Health promoting activities may be attributed to its phenolic constituents: carnosic acid (CA), carnosol (CS), rosmanol (RS) and methyl carnosate (MC), among others [2]. Since dietary phenolic compounds can only produce biological effects upon intestinal absorption, information about such processes is crucial for the evaluation of their potential impact on human health. Due to the morphological and biochemical similarity to normal enterocytes, Caco-2 cell monolayers serve as a well-accepted *in vitro* model for the study of the intestinal absorption potential and transport characteristics of bioactive compounds. In the present work, the permeability of major phenolic compounds present in a supercritical rosemary extract (SC-RE) has been studied using a Caco-2 cell monolayer model (transwell system). In parallel, the intestinal absorption of individual phenolic compounds was also investigated. Bidirectional assay was undertaken to correctly distinguish between those compounds which are reported to undergo active efflux and those which are not. Selective and sensitive identification and quantification of phenolic compounds in the apical and basolateral chambers of the transwell system was achieved by a fast UHPLC-TOF MS method, leading to the determination of apparent permeability values. Overall, our study showed moderate apparent permeability for major phenolic compounds found in SC-RE, suggesting that passive transcellular mechanism may be involved in the basolateral-to-apical transport of these dietary components.

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