ExTech
XXIII

Online event
30th June-2nd July 2021

23rd International Symposium on Advances in Extraction Technologies

Organized by

Universitat d'Alacant
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BOOK OF ABSTRACTS

23rd International Symposium on Advances in Extraction Technologies

Book of abstracts

30th June-2nd July 2021

Title

Book of abstracts - 23rd International Symposium on Advances in Extraction Technologies

Editors

Miguel Ángel Aguirre, Manuel Miró and Lorena Vidal

Book of abstracts

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Online event
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BOOK OF ABSTRACTS

Conference Chair:
Lorena Vidal

Conference co-Chair:
Manuel Miró

Conference Honorary Chair:
Janusz Pawliszyn

Organized by
University of Alicante
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- Analytical and Bioanalytical Chemistry Journal (ABC)-Springer
- Elsevier
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PREFACE

On behalf of the Organizing Committee, it is an honour and a pleasure to welcome you to the 23rd International Symposium on Advances in Extraction Technologies (ExTech).

The ExTech symposium series is the flagship event for sample preparation, analytical extraction and sample clean-up approaches. The series, started in 1999 by Prof. Janusz Pawliszyn (University of Waterloo, Canada), has been annually held around the world. ExTech has become a unique and vital medium for the exchange of information and ideas in the growing field of sample preparation.

The symposium is focused on the fundamentals, developments, and new technologies of extraction and sample preparation in different areas of analytical sciences including new extraction phases and technologies, remote sensing, in-vivo analysis, milli/microfluidics, lab-on-a-chip, diagnostic tool, etc.

The conference consists of a three-day e-meeting involving a total of 277 contributions. The scientific schedule comprises 2 Plenary Lectures, 16 Keynote Lectures, 28 Lectures, 20 Young Lectures, and 11 Lectures given by companies specialised in this field, who sponsored the conference. Additionally, four poster sessions, and virtual exhibitions bringing us up to date on the latest advances and trends in the field are a key part of the conference. Participants also have the opportunity of interacting with the professionals of these companies on all those aspects having such a major impact on our activity.

It is important to highlight that 115 contributions (i.e, posters and oral lectures) are presented by young researchers, who represent the future of this scientific discipline. Furthermore, oral and poster sessions are dedicated to the EuChemS-DAC Study Group and Network.

The Royal Society of Chemistry-Separation Science Group (RSC-SSG), EuChemS-DAC Sample Preparation Study Group and Network, Analytical and Bioanalytical Chemistry Journal (ABC)-Springer, Bruker and Gerstel are sponsoring awards for the best talk and four best poster communications presented by young researchers. The Scientific Committee is in charge of selecting the winners on the basis of both scientific relevance and presentation quality.

A Virtual Special Issue on two Elsevier Journals, Analytica Chimica Acta and Journal of Chromatography A, devoted to the conference will include peer-reviewed manuscripts in accordance with regular journal rules.

We did our best to host the conference in Alicante, known as “City of Light”, which offers an unparalleled combination of liveliness and generosity. Unfortunately, the COVID-19 pandemic situation and the uncertainty around the world forced us to organize it in a virtual modality. However, our main objective is to attain the levels of excellence seen at the previous ExTech meetings. Therefore, we have prepared this important scientific event with a vast amount of effort and dedication, with a view to ensuring a first-rate scientific programme showcasing the latest research and trends in sample preparation.

We hope that you will be able to e-attend and actively participate, and trust that this event will be of the highest scientific and human value, full of content, vibrancy and participation, fulfilling your every expectation.

We look forward to seeing you all at the virtual ExTech2021 conference.

Manuel Miró

Lorena Vidal

Chairs of the 23rd International Symposium on Advances in Extraction Technologies (e-conference)

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GENERAL INFORMATION

Conference address: https://extechvirtual.com/wp-login.php

Login details: Username or e-mail address and password used in the registration process.

Poster communications

There are four poster sessions scheduled in the Scientific Program:

- **POSTER SESSION I: EuChemS-DAC Sample Preparation-Young** (P1-34)
    - Wednesday, 30 June 2021 (13:05-14:00/17:50:18:30)
    - Friday, 2 July 2021 (13:00-14:00)
- **POSTER SESSION II: EuChemS-DAC Sample Preparation** (P35-43)
    - Wednesday, 30 June 2021 (13:05-14:00/17:50:18:30)
    - Friday, 2 July 2021 (13:00-14:00)
- **POSTER SESSION III: General-Young** (P44-P139)
    - Thursday, 1 July 2021 (13:00-14:00)
    - Friday, 2 July 2021 (13:00-14:00)
- **POSTER SESSION IV: General** (P140-P200)
    - Thursday, 1 July 2021 (17:50-18:30)
    - Friday, 2 July 2021 (13:00-14:00)

The posters will be projected in a carousel during the session and the Organizing Committee really appreciates if the corresponding authors of the posters are connected to the platform for zoom chat interaction with other participants. Furthermore, the Scientific Committee will evaluate the Young posters for the best posters Prizes sponsored by EuChemS-DAC Sample Preparation (P1-P34), and sponsored by RSC-SSG, Bruker and Gerstel (P44-P139).

Oral communication sessions

Due to the tight schedule, the Organizing Committee recommends to fit the talk to the fixed time and also to be connected to the platform 10-15 minutes before the session.

SCIENTIFIC PROGRAMME

The programme schedule is given in CET

Wednesday, 30 June 2021

9:00-9:15		**OPENING CEREMONY** **Lorena Vidal, Manuel Miró**
SESSION I. Fundamentals and trends in SPE/SPME **Chairs: Manuel Miró, Lorena Vidal**		
9:15-9:35	KN_01	**ELECTROMEMBRANE EXTRACTION – WHAT IS NEXT?** **Stig Pedersen-Bjergaard** Institute for Pharmacy, University of Oslo (Norway)
9:35-9:55	KN_02	**VACUUM-ASSISTED HEADSPACE MICROEXTRACTION: FASTER, BETTER, EASIER, GENTLER** **Elia Psillakis** Technical University of Crete (Greece)
9:55-10:15	KN_03	**STUDY ON IN VIVO SOLID-PHASE MICROEXTRACTION** **Gangfeng Ouyang** School of Chemistry, Sun Yat-sen University, Guangzhou, (China)
SESSION II. Extraction phases (I) **Chairs: Aristidis Anthemidis, María Llompart**		
10:20-10:40	KN_04	**ZEOLITES AND ZEOLITE-BASED MATERIALS: "OLD" MATERIALS FOR NEW APPLICATIONS IN SAMPLE PREPARATION** **Antonio Canals**, Paola Baile, Elena Fernández, Miguel Ángel Aguirre, Lorena Vidal University of Alicante (Spain)
10:40-10:55	O_01	**FABRICATION OF 6-PHENYLHEXYL SILANE DERIVATIZED, SPUTTERED SILICON SPME FIBERS** **Matthew R. Linford**, Dhananjay I. Patel, George H. Major, Jason Herrington, David S. Bell Brigham Young University (United States)
10:55-11:10	O_02	**HOLISTIC BISPHENOLS ASSESSMENT BY SUPRAMOLECULAR SOLVENT-BASED SAMPLE TREATMENT PLATFORM** **Noelia Caballero-Casero**, Soledad Rubio Universidad de Córdoba (Spain)

11:10-11:25	O_03	**PRE-SCREENING ASSAY BASED ON FAST BLUE B FUNCTIONALIZED SILICA-POLYMER COMPOSITE TO EVALUATE 3,5-DIHYDROXYHYDROCINNAMIC ACID AS BIOMARKER OF GLUTEN INTAKE** **Y. Moliner-Martínez**, L.Hakobyan, M.C. Prieto-Blanco, María Roca Llorens, C. Molins-Legua, P. Campins-Falcó, Carmen Ribes-Koninckx University of Valencia (Spain)
11:25-11:40		**PAUSE**

SESSION III. Young researchers: Material science and environmental applications
Chairs: Enrique J. Carrasco-Correa, Pavel Kuban

11:40-11:50	OY_01	**MAGNETIC IONIC LIQUIDS FOR IMPROVING THE EXTRACTION PERFORMANCE OF ORGANIC POLLUTANTS IN LIQUID-PHASE MICROEXTRACTION** **María J. Trujillo-Rodríguez**, Jared L. Anderson Universidad de La Laguna (Spain)
11:50-12:00	OY_02	**MULTICLASS CYANOTOXIN ANALYSIS IN RESERVOIR WATERS: TANDEM SOLID-PHASE EXTRACTION FOLLOWED HYDROPHILIC INTERACCION LIQUID CHROMATOGRAPHY- MASS SPECTROMETRY** **M. Mar Aparicio-Muriana**, Francisco J. Lara, Ana M. García-Campaña, Monsalud del Olmo-Iruela University of Granada (Spain)
12:00-12:10	OY_03	**NOVEL EXTRACTION METHOD FROM WET HAEMATOCOCCUS PLUVIALIS USING GRAS SOLVENTS VIA MATRIX SOLID-PHASE DISPERSION** **Aly Castillo**, Marta Lores, Carmen Garcia-Jares Universidade de Santiago de Compostela (Spain)

SESSION III (cont). Young researchers: Environmental and food applications
Chairs: Miguel Ángel Aguirre, Mariosimone Zoccali

12:15-12:25	OY_04	**IN-VITRO HUMAN ORAL BIOACCESIBILITY OF PLASTICIZERS FROM MICROPLASTICS UNDER SIMULATED GASTRO-INTESTINAL DIGESTION** **J. López-Vázquez**, J.B. Quintana, M. Trujillo, R. Cela, R. Rodil, M. Miró University of Santiago de Compostela (Spain)
12:25-12:35	OY_05	**NATURAL DEEP EUTECTIC SOLVENTS FOR GREEN MICROWAVE-ASSISTED EXTRACTION OF ACTIVE COMPOUNDS FROM "HORCHATA DE CHUFA" BY-PRODUCTS** **Carlos Javier Pelegrín**, Alfonso Jiménez, María del Carmen Garrigós University of Alicante (Spain)

12:35-12:45	OY_06	**NON-TARGET SCREENING OF PHAMARCEUTICALS IN SEWAGE SLUDGE: COMPARISON BETWEEN DDA AND DIA ANALYSIS** **G. Castro**, M. Ramil, R. Cela, I. Rodríguez University of Santiago de Compostela (Spain)
12:45-12:55	OY_07	**ASSESSMENT OF ION IMPRINTED POLYMERS TECHNOLOGY FOR THE DESIGN OF A NEW RADIUM SPECIFIC SOLID PHASE EXTRACTION SUPPORT** **Marine Boudias**, Alkiviadis Gourgiotis, Charlotte Cazala, Valérie Pichon, Nathalie Delaunay Ecole Superieure de Physique et Chimie Industrielle (ESPCI) (France)
12:55-13:05	OY_08	**COMBINING PRESSURIZED LIQUID EXTRACTION AND ENZYMATIC-ASSISTED EXTRACTION TO OBTAIN BIOACTIVE NON-EXTRACTABLE POLYPHENOLS FROM SWEET CHERRY (PRUNUS AVIUM L.) POMACE** **Gloria Domínguez-Rodríguez**, María Concepción García, Merichel Plaza, María Luisa Marina University of Alcala (Spain)
13:05-14:00		**PAUSE & POSTER SESSIONS I & II**

SESSION IV. EuChemS-DAC Sample Preparation-Young

Chairs: Elia Psillakis, Antonio Canals

14:00-14:10	OYEu_01	**PREPARATION AND EVALUATION OF MIXED-MODE MATERIALS TO SELECTIVELY EXTRACT ACIDIC COMPOUNDS BY STIR BAR SORPTIVE EXTRACTION FROM ENVIRONMENTAL WATERS** **J.C. Nadal**, M. Catalá-Icardo, F. Borrull, J.M. Herrero-Martínez, R.M. Marcé, N. Fontanals Universitat Rovira i Virgili (Spain)
14:10-14:20	OYEu_02	**THIN-FILM MICROEXTRACTION USING MOF-BASED POLYMERIC COMPOSITES AND LIQUID CHROMATOGRAPHY FOR THE DETERMINATION OF PERSONAL CARE PRODUCTS IN COSMETICS** **Adrián Gutiérrez-Serpa**, Jorge Pasán, Ana Isabel Jiménez-Abizanda, Francisco Jiménez-Moreno, Stefan Kaskel, Verónica Pino Universidad de La Laguna (Spain)
14:20-14:30	OYEu_03	**PROFILING OF CARNITINE AND ACYLCARNITINES IN GLIOMAS USING SOLID PHASE MICROEXTRACTION (SPME) –THE PILOT STUDY** **Joanna Bogusiewicz**, Katarzyna Burlikowska, Karol Jaroch, Paulina Zofia Gorynska, Krzysztof Gorynski, Marcin Birski, Jacek Furtak, Dariusz Paczkowski, Marek Harat, Barbara Bojko Nicolaus Copernicus University (Poland)
14:30-14:40	OYEu_04	**NEW TRENDS IN FOOD ANALYSIS BASED ON MICROEXTRACTIONS THECNIQUES** **J. A. Custodio-Mendoza**, L. Muñoz-Menendez, A. M. Carro, R. A. Lorenzo University of Santiago de Compostela (Spain)

14:40-14:50	OYEu_05	**APPLICATION OF VACUUM-ASSISTED HEADSPACE SOLID PHASE MICROEXTRACTION TO CHARACTERISE THE VOLATILE AND SEMI-VOLATILE FRACTIONS OF COMPLEX SOLID PLANT MATRICES** **Francesca Capetti**, Giulia Mastellone, Patrizia Rubiolo, Carlo Bicchi, Arianna Marengo, Barbara Sgorbini, Elefteria Psillakis, Cecilia Cagliero Università di Torino (Italy)

SESSION V. Biological and food analysis
Chairs: Stig Pedersen-Bjergaard, Burkhard Horstkotte

14:55-15:15	OC_01	**NEEDLE TRAP MICRO EXTRACTION (NTME) – A COMBINED POC SAMPLING & PRE CONCENTRATION TECHNIQUE FOR VOC PROFILES IN BIOMEDICAL ANALYSIS** **Julia Bartels,** Wolfram Miekisch, Jochen K. Schubert University Medicine of Rostock (Germany)
15:15-15:35	OC_02	**A NEW APPROACH TO FAT DETERMINATION IN FOOD AND FEED SAMPLES USING MICROWAVE ASSISTED EXTRACTION** **Roberto Boschini,** Giulio Colnaghi, Diego Carnaroglio Milestone Srl
15:35-15:50	O_04	**CAPILLARY ELECTROPHORESIS FOR THE AUTOMATED EXTRACTION AND ANALYSIS OF DRIED BLOOD SPOTS IN CLINICAL ANALYSIS** **Pavel Kubáň**, Lenka Ryšavá, Miloš Dvořák Institute of Analytical Chemistry of the Czech Academy of Sciences, Brno (Czech Republic)
15:50-16:05	O_05	**ON-LINE SOLID-PHASE EXTRACTION CAPILLARY ELECTROPHORESIS-MASS SPECTROMETRY WITH A NANOLITER VALVE FOR THE ANALYSIS OF PEPTIDE BIOMARKERS** **Fernando Benavente**, Roger Pero-Gascon, Christian Neusüß, Victoria Sanz-Nebot University of Barcelona (Spain)
16:05-16:20	O_06	**FIBREATHALYZER-4000 A USEFUL DEVICE FOR ANALYSIS OF COVID-19 IN EXHALED BREATH- AN ASCEDENT PROPOSAL** **Milton Rosero-Moreano**, Álvaro Pulzara-Mora, John Ríos-Acevedo, Diego Montaño-Montoya Universidad de Caldas (Colombia)
16:20-16:35	O_07	**AUTOMATED HIGH-THROUGHPUT MEASUREMENT OF PROTEIN BINDING USING SOLID PHASE MICROEXTRACTION AND LC-MS/MS** **Olga I. Shimelis**, M. James Ross, Hugh Cramer, Teresa Marsala, Candace Price MilliporeSigma, Bellefonte (USA)

16:35-16:50	O_08	**HS-SPME-MS AS A TOOL FOR RAPID AUTHENTICITY AND QUALITY CONTROL OF ALCOHOLIC BEVERAGES** **Henryk H. Jeleń**, Xi He, Małgorzata Majcher Poznań UNiversity of Life Sciences (Poland)

SESSION VI. Fundamentals and applications of SPME
Chairs: Jared Anderson, José Manuel Nogueira

17:00-17:30	PL_01	**SPME DEVICE DESIGN AND METHOD OPTIMIZATION USING FUNDAMENTALS** **Janusz Pawliszyn** University of Waterloo (Canada)
17:30-17:50	KN_05	**HEADSPACE SOLID PHASE MICROEXTRACTION APPLIED TO ANALYSIS OF COMPOUNDS WITH LOW VOLATILITY** **Fabio Augusto** University of Campinas (Brazil)
17:50-18:30		**POSTER SESSIONS I & II**

Thursday, 1 July 2021

SESSION VII. Microextraction approaches
Chairs: Valérie Pichon, José Manuel Herrero

9:00-9:20	KN_06	**MICRODROP LIQUID-PHASE MICROEXTRACTION (SINGLE-DROP MICROEXTRACTION): COMING FULL CIRCLE?** **Hian Kee Lee** National University of Singapore (Singapore)
9:20-9:40	KN_07	**SIMPLICITY, SUSTAINABILITY, AND SYNERGY: THE 3-S COMMITMENT OF CELLULOSIC SUPPORTS TO SAMPLE PREPARATION** **Soledad Cárdenas** Universidad de Córdoba (Spain)
9:40-10:00	KN_08	**DIFFERENT ANALYTICAL APPROACHES FOR EVALUATING THE ENVIRONMENTAL AND HEALTH IMPACTS OF RECYCLED CRUMB RUBBER USED IN RECREATIONAL AND SPORTS SURFACES** **Maria Llompart**, Daniel Armada, Antia Martinez, Pablo Garcia, Maria Celeiro, Thierry Dagnac Universy of Santiago de Compostela (Spain)
10:00-10:15	O_09	**DISPERSIVE LIQUID-LIQUID MICROEXTRACTION COMBINED WITH PLASMA-BASED SPECTROMETRY DETECTION: PAST, PRESENT AND FUTURE** Daniel Torregrosa, David Lledó, Raquel Serrano, **Guillermo Grindlay**, Luis Gras, Juan Mora University of Alicante (Spain)
10:15-10:30	O_10	**TOWARDS THE KNOWLEDGE OF NANOSCALE INTERACTIONS IN THE CONTEXT OF LIQUID CHROMATOGRAPHY: NEW OPPORTUNITIES FOR/FROM NANOSCALE AND LC** **P. Campíns-Falcó**, Y. Moliner-Martínez, C. Molins-Legua, R. Herráez-Hernández University of Valencia (Spain)
10:30-10:45	O_11	**SAMPLE PREPARATION UNDER TURBULENT FLOW WITH RENEWABLE SORBENT** **David J. Cocovi-Solberg**, Stephan Schnidrig, Manuel Miró, Stephan Hann University of Natural Resources and Life Sciences in Vienna (Austria)
10:45-11:05	OC_03	**NEW MOBILITY DIMENSION FOR THE ANALYSIS OF PRIORITY HAZARDOUS SUBSTANCES IN WATER BY TISMTOF** Miguel Angel Pérez, Diego Martín-Ortiz, Javier López, **Pedro Cano** Bruker Application Development Laboratory and Bruker Española S.A., Madrid (Spain)
11:05-11:30		**PAUSE**

SESSION VIII. EuChemS-DAC Sample Preparation
Chairs: Rafael Lucena, Giorgia Purcaro

11:30-11:45	OEu_01	**FROM PLANTS SAMPLES TO ANALYSIS OF BIOLOGICALLY ACTIVE COMPOUNDS – TOWARD GREEN(ER) ANALYTICAL CHEMISTRY** **Slavica Ražić**, Aleksandra Cvetanović, Jelena Arsenijević University of Belgrade (Serbia)
11:45-12:00	OEu_02	**DEVELOPMENT OF HYBRID MONOLITHS INCORPORATING METAL-ORGANIC FRAMEWORKS FOR STIR BAR SORPTIVE EXTRACTION COUPLED WITH HPLC FOR DETERMINATION OF ESTROGEN ENDOCRINE DISRUPTORS IN ENVIRONMENTAL AND BIOLOGICAL SAMPLES** Héctor Martínez-Pérez-Cejuela, Slavomíra Zatrochová, Dalibor Šatinský, Mónica Catalá-Icardo, Ernesto F. Simó-Alfonso, **José Manuel Herrero-Martínez** University of Valencia (Spain)
12:00-12:15	OEu_03	**IN-SYRINGE AUTOMATION OF SAMPLE PREPARATION FOR ENVIRONMENTAL ANALYSIS** **Burkhard Horstkotte**, Kateřina Fikarová, Ivana H. Šrámková, Celestine Gemuh Vubangsi, Hana Sklenářová, Petr Solich Charles University (Czech Republic)
12:15-12:30	OEu_04	**RECENT ACHIEVEMENTS IN VERSATILITY THROUGH STIR BAR SORPTIVE DISPERSIVE MICROEXTRACTION APPROACH** **Alberto Chisvert**, Juan L. Benedé, José Grau, Víctor Vállez-Gomis, Cristian Azorín, Amparo Salvador University of Valencia (Spain)
12:30-12:45	OEu_05	**ON-LINE SFE-ENANTIOSELECTIVE-SFC-QQQ MS FOR THE DETERMINATION OF CHIRAL PESTICIDES IN HEMP SEEDS: A PROOF-OF-PRINCIPLE STUDY** **Mariosimone Zoccali**, Marina Russo , Mariarita Testa Camillo , Luigi Mondello University of Messina (Italy)
12:45-13:00	OEu_06	**QUANTITATION OF TRANSFORMATION PRODUCTS OF UNSYMMETRICAL DIMETHYLHYDRAZINE IN SAND USING VACUUM-ASSISTED HEADSPACE SOLID-PHASE MICROEXTRACTION** Aray Zhakupbekova, **Nassiba Baimatova**, Elefteria Psillakis, Bulat Kenessov Al-Farabi Kazakh National University (Kazakhstan)
13:00-14:00		**PAUSE & POSTER SESSION III**

SESSION IX. EuChemS-DAC Sample Preparation

Chairs: Marcela Segundo, Slavica Ražić

14:00-14:15	OEu_07	**IN-SITU EXTRACTION APPROACHES FOR ENVIROMENTAL WATERS ANALYSIS** **R. Lucena**, F. A. Casado-Carmona, S. Cárdenas Universidad de Córdoba (Spain)
14:15-14:30	OEu_08	**MULTI-CUMULATIVE TRAPPING HS-SPME: A NOVEL APPROACH TO ENHANCE VOLATILE FINGERPRINTING** S. Mascrez, **G.Purcaro** University of Liège (Belgium)
14:30-14:45	OEu_09	**CHEMICAL MODIFICATION OF 3D PRINTED STRUCTURES WITH SMART MATERIALS FOR SAMPLE PREPARATION** **Enrique Javier Carrasco-Correa**, Ernesto Francisco Simó-Alfonso, José Manuel Herrero-Martínez, Manuel Miró University of Valencia (Spain)
14:45-15:00	OEu_10	**SYNERGISTIC COMBINATION OF POLYAMIDE-COATED PAPER-BASED SORPTIVE PHASE FOR THE EXTRACTION OF ANTIBIOTICS IN SALIVA** **Juan L. Benedé**, Alberto Chisvert, Rafael Lucena, Soledad Cárdenas University of Valencia (Spain)

SESSION X. Clinical and biological analysis

Chairs: Pilar Campins, Fernando Benavente

15:05-15:25	KN_09	**HIGH THROUGHPUT NUCLEIC ACID SAMPLE PREPARATION AND ANALYSIS** **Jared L. Anderson**, Marcelino Varona, Miranda Emaus, Derek Eitzmann Iowa State University (USA)
15:25-15:45	KN_10	**SPME-BASED SAMPLE PREPARATION STRATEGIES IN CLINICAL AND BIOMEDICAL ANALYSIS** **Anna Roszkowska,** Joanna Bogusiewicz, Paulina Zofia Goryńska, Kamil Łuczykowski, Katarzyna Burlikowska, Karol Jaroch, Krzysztof Goryński, Marcin Birski, Dariusz Paczkowski, Jacek Furtak, Marek Harat, Tomasz Bączek, Janusz Pawliszyn, Barbara Bojko Nicolaus Copernicus University (Poland)
15:45-16:05	KN_11	**BEAD INJECTION LAB-ON-VALVE AUTOMATION FOR AFFINITY BASED SEPARATIONS** **Marcela A. Segundo**, Sara S. Marques, Inês I. Ramos, Luisa Barreiros University of Porto (Portugal)

16:05-16:25	OC_04	**USING ACCELERATED SOLVENT EXTRACTION TO UNCOVER SUBSTANCES OF TOXICOLOGICAL INTEREST IN BONES AND BLOOD SAMPLES** **Fabrizio Galbiati** Thermo Fisher Scientific
16:25-16:45	OC_05	**NATURAL PRODUCT PREPARATIVE SEPARATIONS BY CENTRIFUGAL PARTITION CHROMATOGRAPHY (CPC)** **Grégoire Audo** Gilson

SESSION XI. Young researchers: Pharmaceutical and biological applications

Chairs: Yolanda Moliner, David J. Cocovi

16:50-17:00	OY_09	**SAMPLE TREATMENT STRATEGIES BASED ON LAB-ON-VALVE FOR DETERMINATION OF BIOACTIVE COMPOUNDS IN BIOMATRICES** **Sara R. Fernandes**, Luisa Barreiros, Manuel Miró, Marcela A. Segundo University of Porto (Portugal)
17:00-17:10	OY_10	**PAPER-BASED MICROFLUIDIC DEVICES AS EFFECTIVE EXTRACTION METHOD FOR NUCLEIC ACID BASED PATHOGEN DETECTION FOR WATER QUALITY** **Yuwei Pan,** Zhugen Yang Cranfield University (UK)
17:10-17:20	OY_11	**ELECTROMEMBRANE EXTRACTION OF POLAR SUBSTANCES – CURRENT STATUS AND FUTURE PERSPECTIVES** **Frederik André Hansen**, Stig Pedersen-Bjergaard University of Oslo (Norway)
17:20-17:30	OY_12	**ELECTROMEMBRANE EXTRACTION OF PHARMACEUTICALS AND ENDOGENOUS METABOLITES WITH CHITOSAN TAILOR-MADE MEMBRANES AS BIOPOLYMERIC SUPPORT** **Cristina Román-Hidalgo**, Noemí Aranda-Merino, Mercedes Villar-Navarro, Juan Luis Pérez-Bernal, Germán López-Pérez, MªJesús Martín-Valero, Miguel Ángel Bello-López Universidad de Sevilla (Spain)
17:30-17:40	OY_13	**A NEW VALIDATED WIPE SAMPLING PROCEDURE COUPLED TO LC-MS/MS FOR ASSESSING SURFACE CONTAMINATION BY 13 CYTOSTATICS** **M. Francisca Portilha-Cunha**, Sara Ramos, Adrián M. T. Silva, Pedro Norton, Arminda Alves, Mónica S. F. Santos University of Porto (Portugal)

17:40-17:50	OY_14	**ANALYSIS OF MICROBIAL CONTAMINATED COSMETIC CREAMS BY ION MOBILITY SPECTROMETRY AND MASS SPECTROMETRY COUPLED TO GAS CHROMATOGRAPHY** **María García-Nicolás**, Natalia Arroyo-Manzanares, Juan de Dios Hernández, Isidro Guillén, Pascuala Vizcaíno, Marta Sánchez-Rubio, Ignacio López-García, Manuel Hernández-Córdoba, Pilar Viñas University of Murcia (Spain)
17:50-18:30		**POSTER SESSION IV**

Friday, 2 July 2021

SESSION XII. Extraction technologies for organics
Chairs: José Benito Quintana, Verónica Pino

9:00-9:20	KN_12	**CONSIDERATIONS AND FUTURE TRENDS ON PASSIVE MICROEXTRACTION TECHNIQUES** **José Manuel Nogueira** Universidade de Lisboa (Portugal)
9:20-9:40	KN_13	**MIGRATION OF (SEMI-)VOLATILE ORGANIC COMPOUNDS INTO FOOD SIMULANTS FROM PLASTIC FOOD CONTAINERS AND MOLDS** J. Bintanel-Cenís, C. Fernández-Ramos, A. Gil-Asenjo, C. Carrero-Carralero, J. Escobar-Arnanz, B. Gómora, **Lourdes Ramos** Dpt. Instrumental Analysis and Environmental Chemistry, IQOG-CSIC, Madrid (Spain)
9:40-9:55	O_12	**CRITICAL EVALUATION (OPTIMISATION) OF ANALYTICAL EXTRACTION OF PLASTICISERS IN FOOTWEAR MATERIALS** **Gemma Rubio**, Ana Torró, Elena Orgilés, Luis Gras, Guillermo Grindlay University of Alicante (Spain)
9:55-10:15	OC_06	**NON-TARGET IDENTIFICATION OF POLAR ORGANICS IN CIGARETTE LEACHATE BY HIGH-CAPACITY SORTIVE EXTRACTION AND TD-GC×GC–TOF MS** David Bowman, Rachael Szafnauer, **Laura McGregor,** Elia Psillakis SepSolve Analytical (UK)
10:15-10:35	OC_07	**NEEDLETRAP – A UNIVERSAL TOOL FOR A WIDE RANGE OF APPLICATION FOR VOC-ANALYSIS** **Dietmar Hein** PAS Technology Deutschland GmbH
10:35-10:55	OC_08	**COMPARISON OF VOLATILE ORGANIC COMPOUNDS EXTRACTION TECHNIQUES FOR THE COMPREHENSIVE CHARACTERISATION OF TOMATO PRODUCTS** **Natasha D. Spadafora**, Rachael Szafnauer, Laura McGregor, Nick Bukowski University of Calabria (Italy)
10:55-11:15	OC_09	**MICROWAVE ASSISTED EXTRACTION A POWERFUL AND GREENER APPROACH FOR ENVIRONMENTAL SAMPLES, FOOD ANALYSIS AND ESSENTIAL OILS EXTRACTION** **Roberto Boschini,** Giulio Colnaghi, Diego Carnaroglio Milestone Srl
11:15-11:30		**PAUSE**

SESSION XIII. Extraction phases (II)
Chairs: Soledad Cárdenas, Henryk Jelen

11:30-11:50	KN_14	**POTENTIAL OF IMPRINTED POLYMERS FOR THE SELECTIVE EXTRACTION OF TARGET MOLECULES AND METAL IONS FROM COMPLEX SAMPLES** Nathalie Delaunay, Pengchao Cao, Audrey Combès, **Valérie Pichon** Ecole Superieure de Physique et Chimie Industrielle (ESPCI) (France)
11:50-12:10	KN_15	**NOVEL MATERIALS IN ANALYTICAL SAMPLE PREPARATION: WHERE ARE WE GOING?** **Verónica Pino**, Idaira Pacheco-Fernández, Adrián Gutiérrez-Serpa, Iván Taima-Mancera, Raúl González-Martín, Diego W. Allgaier-Díaz, Ana B. Lago, Juan H. Ayala, Jorge Pasán Universidad de La Laguna (Spain)
12:10-12:25	O_13	**EXPLORING THE APPLICATION OF SELF-IMMOLATIVE POLYMERS IN SAMPLE PREPARATION** Cecilia Ortega-Zamora, Javier González-Sálamo, David Santana, Romen Carrillo, **Javier Hernández-Borges** Universidad de La Laguna (Spain)
12:25-12:40	O_14	**A SIMPLE METHODOLOGY BASED ON POLYMER INCLUSION MEMBRANES AND XRF ANALYSIS FOR THE MONITORING OF METALS IN NATURAL WATERS** **Clàudia Fontàs**, Berta Alcalde, Nora Serrat, Enriqueta Anticó, Eva Marguí University of Girona (Spain)
12:40-13:00	OC_10	**MEET THE #CONNECTEDLABORATORY** **Evelien Dejaegere** Waters
13:00-14:00		**PAUSE & POSTER SESSIONS I, II, III & IV**

SESSION XIV. Environmental analysis
Chairs: Lourdes Ramos, Alberto Chisvert

14:00-14:20	KN_16	**ANALYSIS OF MICROPLASTICS IN WATER: FOCUS ON SAMPLING, SAMPLE PREPARATION AND GREEN ANALYTICAL PROTOCOLS** **Damià Barceló,** Yolanda Picó IDAEA-CSIC, Barcelona (Spain) & Catalan Institute for Water Research (ICRA-CERCA) Girona (Spain)

14:20-14:40	OC_11	**DETERMINATION OF MICROPLASTICS IN WATER AND ENVIRONMENTAL MATRICES COMBINING THERMAL DEGRADATION WITH SOLID PHASE EXTRACTION AND GC/MS DETERMINATION OF POLYMER DEGRADATION PRODUCTS** **Kaj Petersen,** Eike Kleine-Benne GERSTEL GmbH &Co.KG
14:40-14:55	O_15	**MOLECULARLY IMPRINTED POLYMERS FOR THE SELECTIVE EXTRACTION OF ENVIRONMENTAL CONTAMINANTS** **A. Barranco**, A. Ereño Artabe, H. Cunha-Silva AZTI, Food Research, Basque Research and Technology Alliance (BRTA) (Spain)
14:55-15:10	O_16	**PARALLEL ARTIFICIAL LIQUID MEMBRANE EXTRACTION OF ORGANOPHOSPHORUS NERVE AGENT DEGRADATION PRODUCTS FROM ENVIRONMENTAL SAMPLES** **Khirreddine Bouchouareb**, Audrey Combes, Valérie Pichon Ecole Superieure de Physique et Chimie Industrielle (ESPCI) (France)
15:10-15:25	O_17	**AN EASY-TO-PERFORM ANALYTICAL METHOD FOR THE DETERMINATION OF IBUPROFEN AND ITS MAIN METABOLITES IN MARINE BIVALVES** **Irene Aparicio**, Juan Luis Santos, Julia Martín, Tainá Garcia da Fonseca, María João Bebianno, Esteban Alonso Universidad de Sevilla (Spain)
15:25-15:40	O_18	**VOLATILE METHYL SILOXANES IN WASTEWATER TREATMENT PLANTS: ANALYSIS AND QUANTIFICATION** Francisco Sánchez-Soberón, Madalena Fernandes, Diogo Bogas, Ana Catarina Rodrigues, Gabriel F. Pantuzza, Fábio Bernardo, Idalina Bragança, Arminda Alves, Vera Homem, **Nuno Ratola** University of Porto (Portugal)

CLOSING LECTURE

Chairs: Lorena Vidal, Manuel Miró

15:50-16:20	PL_02	**ECO-EFFICIENT ANALYTICAL METHODOLOGIES USING ROTATING-DISK SORPTIVE EXTRACTION** **Pablo Richter** Universidad de Chile, (Chile)
16:30		**CLOSING CEREMONY & AWARDS** **Lorena Vidal, Manuel Miró**

POSTER SESSION I: EuChemS-DAC Sample Preparation-Young

Wednesday, 30 June 2021 (13:05-14:00/17:50:18:30)
Friday, 2 July 2021 (13:00-14:00)

P1 **MINIATURIZED AQUEOUS BIPHASIC SYSTEM CONSISTING OF FOOD ADDITIVES FOR THE PRECONCENTRATION OF PERSONAL CARE PRODUCTS IN WASTEWATERS**
Jakub Šulc, Idaira Pacheco-Fernández*, Juan H. Ayala, Petra Bajerová, Verónica Pino

P2 **NATURAL DEEP EUTECTIC SOLVENT (NADES) AS A NOVEL DISPERSER IN LIQUID–LIQUID MICROEXTRACTION BASED ON SOLIDIFICATION OF FLOATING ORGANIC DROPLET (DLLME-SFO)**
Laura Carbonell-Rozas*, Romina Canales, Francisco J. Lara, Ana M. García Campaña, María Fernanda Silva

P3 **THE INFLUENCE OF DISINTEGRATION METHOD TO THE EXTRACTION EFFICIENCY IN METABOLOMICS ANALYSIS**
Karolina Anna Mielko*, Sławomir Jabłoński, Marcin Łukaszewicz, Piotr Młynarz

P4 **VOLATILE PROFILING BY SPME GC-MS FOR AUTHENTICATION OF GREEN TEA (CAMELLIA SINENSIS) SAMPLES AND SUPPLEMENTS**
I. Luque-Jurado*, S. Rivas, M.L. Sanz, M. Fernández, A.C. Soria

P5 **ANALYTICAL PLATFORM FOR THE STUDY OF PTSO METABOLIC PATHWAY**
María García-Nicolás*, Marta Pastor-Belda, Natalia Arroyo-Manzanares, Natalia Campillo, P. Abad, A. Baños, J.M. de la Torre, Pilar Viñas

P6 **HYPHENATION AND MULTIDIMENSIONALITY AS SAMPLE PREPARATION ALLEYS IN MOSH AND MOAH ANALYSIS**
G.Bauwens*, G.Purcaro

P7 **QUANTIFICATION AND CHARACTERIZATION OF MINERAL OIL IN FISH FEED BY LC-GC×GC-TOFMS/FID**
G.Bauwens*, G.Purcaro

P8 **SUSTAINABLE MICRO-SCALE EXTRACTION OF BIOACTIVE PHENOLIC COMPOUNDS FROM VITIS VINIFERA LEAVES WITH IONIC LIQUID-BASED SURFACTANTS**
Giulia Mastellone*, Idaira Pacheco-Fernández, Patrizia Rubiolo, Verónica Pino, Cecilia Cagliero

P9 **ENHANCING THE VOLATILE PROFILE AT SUB-AMBIENT TEMPERATURE BY USING VACUUM-ASSISTED HS-SPME. CASE STUDY ON FISH SPOILAGE**
S.Mascrez*, E. Psillakis, G. Purcaro

P10 **EXPLORING THE CAPABILITY OF THE HISORB PROBE FOR CHARACTERIZATION OF VOLATILE AND SEMI-VOLATILE COMPOUNDS IN BREWED COFFEE BY GCXGC-QMS**
S.Mascrez*, D. Eggermont, G. Purcaro

P11 **LAB-IN-SYRINGE AUTOMATED SAMPLE PREPARATION PROCEDURES BASED ON HOMOGENEOUS LIQUID-LIQUID EXTRACTION**
Kateřina Fikarová*, Daniel Machián, Hana Sklenářová, Burkhard Horstkotte

P12 **LEACHING OF PAHS FROM HEAT-NOT-BURN TOBACCO PRODUCTS AND CIGARETTE BUTTS**
N. Solomou*, E. Fernandez, R. Szafnauer, E. Psillakis

P13 **UV-254 DEGRADATION OF NICOTINE IN NATURAL WATERS AND LEACHATES PRODUCED FROM CIGARETTE BUTTS AND HEAT-NOT-BURN TOBACCO PRODUCTS**
N. Solomou*, S. Alberti, M. Sotiropoulou, E. Fernandez, M. Ferretti, R. Szafnauer, E. Psillakis

P14 **LAB-MADE STIRRING EXTRACTION UNIT BASED ON CARBON NANOTUBE-MOLECULARLY IMPRINTED MONOLITHS**
Beatriz Fresco-Cala*, Soledad Cárdenas

P15 **MAGNETIC SOLIDS BASED ON CARBON NANOTUBES PREPARED FROM PICKERING EMULSIONS**
Beatriz Fresco-Cala*, Ana Gálvez-Vergara, Soledad Cárdenas

P16 **DEVELOPMENT AND VALIDATION OF METHODS USING SOLID-PHASE EXTRACTION, OFFLINE DERIVATIZATION AND UHPLC-ESI(+)-MS/MS FOR THE QUANTIFICATION OF ESTROGENIC COMPOUNDS AT ULTRA-TRACE LEVELS IN DIFFERENT TYPES OF WATER**
Alex Glineur*, Katherine Nott, Giorgia Purcaro

P17 **COMPUTER FAN'S POTENTIAL IN AIR SAMPLING**
Francisco Antonio Casado-Carmona*, Guillermo Lasarte-Aragonés, Abuzar Kabir, Kenneth G. Furton, Rafael Lucena, Soledad Cárdenas

P18 **COMPOSITES BASED ON METAL-ORGANIC FRAMEWORKS AND THEIR POTENTIAL APPLICATION IN DISPERSIVE MICRO-SOLID-PHASE EXTRACTION**
Patricia I. Napolitano-Tabares*, Adrián Gutiérrez-Serpa, Ana I. Jiménez-Abizanda, Francisco Jiménez-Moreno, Jorge Pasán, Verónica Pino

P19 FABRIC PHASE SORPTIVE EXTRACTION OF SELECTED POLYCYCLIC AROMATIC HYDROCARBONS FROM HERBAL INFUSIONS AND TEA SAMPLES FOLLOWED BY ANALYSIS USING GAS CHROMATOGRAPHY-MASS SPECTROMETRY

N. Manousi*, A. Kabir, K. G. Furton, E. Rosenberg, G. A. Zachariadis

P20 A MONOLITHIC CAPSULE PHASE MICROEXTRACTION PLATFORM COMBINED WITH HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-DIODE ARRAY DETECTION FOR THE MONITORING OF TRIAZINE HERBICIDES IN WATER SAMPLES

N. Manousi*, V. Alampanos, I. Priovolos, A. Kabir, K. G. Furton, E. Rosenberg, G. A. Zachariadis, V. F. Samanidou

P21 A SOL-GEL ZWITTERIONIC MIXED-MODE PLATFORM FOR THE FABRIC PHASE SORPTIVE EXTRACTION OF TRIAZINE HERBICIDES FROM FRUIT JUICE SAMPLES

V. Alampanos*, N. Manousi , A. Kabir , K. G. Furton, E. Rosenberg , G. A. Zachariadis , V. F. Samanidou

P22 MAGNET INTEGRATED FABRIC PHASE SORPTIVE EXTRACTION OF SELECTED ENDOCRINE DISRUPTING CHEMICALS FROM HUMAN URINE PRIOR TO HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY – PHOTODIODE ARRAY ANALYSIS

V. Alampanos*, A. Kabir, K. G. Furton, V. Samanidou

P23 MICROWAVE ASSISTED EXTRACTION AS A PROMISING TECHNIQUE FOR EXTRACTION OF BIOACTIVE CARBOHYDRATES FROM VEGETABLE BY-PRODUCTS

Adal Mena-García*, María Luz Sanz, Ana Cristina Soria, Marina Díez Municio, Ana Isabel Ruiz-Matute

P24 A POLY(METHACRYLIC ACID-ETHYLENE GLYCOL DIMETHACRYLATE) MAGNETIC COMPOSITE FOR TRACE DETERMINATION OF TRICYCLIC ANTIDEPRESSANTS AND THEIR ACTIVE METABOLITES IN HUMAN URINE BY STIR BAR SORPTIVE DISPERSIVE MICROEXTRACTION

Víctor Vállez-Gomis*, Sara Exojo, Juan L. Benedé, Alberto Chisvert, Amparo Salvador

P25 TRACE DETERMINATION OF TETRAHYDROCANNABINOL (THC) IN COSMETIC PRODUCTS BY STIR BAR SORPTIVE DISPERSIVE MICROEXTRACTION-LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY

Cristian Azorín*, Juan L. Benedé, Alberto Chisvert, Amparo Salvador

P26 PROFILING NAPHTHENIC ACIDS IN PRODUCED WATER USING HOLLOW FIBER LIQUID PHASE MICROEXTRACTION COMBINED WITH GAS CHROMATOGRAPHY COUPLED TO FOURIER TRANSFORM ORBITRAP MASS SPECTROMETRY

Nathália de Aguiar Porto*, Juliana Crucello, Roselaine Facanali, Rogerio Mesquita de Carvalho, Iris Medeiros Junior, Leandro Wang Hantao

P27 MODIFIED MAGNETIC-BASED SOLVENT ASSISTED DISPERSIVE SOLID-PHASE EXTRACTION FOR THE DETERMINATION OF CORTISOL AND CORTISONE IN HUMAN SALIVA

José Grau*, Juan L. Benedé, Alberto Chisvert, Amparo Salvador

P28 IN-DEPTH EVALUATION OF METAL-ORGANIC FRAMEWORKS AS SORBENTS IN ANALYTICAL MICROEXTRACTION: ADSORPTION AND KINETIC STUDIES

Iván Taima-Mancera*, Norberto Medina, Adrián Gutiérrez-Serpa, Jorge Pasán, Verónica Pino

P29 OPTIMIZATION OF VAC-HSSPME+GC–MS FOR DETERMINATION OF BIOMARKER PROFILES ON OIL SOURCE ROCKS USING MULTIVARIATE APPROACHES

Breno Jorge Pollo*, Paulo de Tarso Vieira e Rosa, Fabio Augusto

P30 DISPERSIVE LIQUID-LIQUID MICROEXTRACTION FOR SIMULTANEOUS DETERMINATION OF MALONDIALDEHYDE, ACROLEIN AND 4-HIDROXY-2-NONENAL IN BEVERAGES BY GC-MS

J. A. Custodio-Mendoza*, C. Caamano-Fernandez, A. M. Carro, R. A. Lorenzo

P31 DEVELOPMENT AND APPLICATION OF A MINIATURIZED ACTIVE AIR SAMPLING METHOD FOR INDOOR AND OUTDOOR PLACES ADJANCENT TO SURFACES MADE OF TIRE RUBBER

Antía Martínez-Fernández*, Daniel Armada, Laura Conde, María Celeiro, Piyaluk Nurerk, Thierry Dagnac, María Llompart

P32 DETERMINATION OF FUNGICIDES IN SEVERAL MATRICES BY DIFFERENT EXTRACTION TECHNIQUES

Lúa Vazquez*, María Celeiro, Meruyert Sergazina, Thierry Dagnac, María Llompart*

P33 SYNTHESIS AND CHARACTERIZATION OF ZWITTERIONIC POLYMERIC IONIC LIQUID SORBENT FOR FIBER-IN-TUBE SPME TANDEM MASS SPECTROMETRY TO DETERMINE ALZHEIMER'S DISEASE BIOMARKER

Israel D. Souza*, Jared L. Anderson and Maria Eugênia Costa Queiroz

P34 SYNTHESIS AND CHARACTERIZATION OF A MONOLITHIC STATIONARY PHASE WITH SULFONIC GROUPS FOR IN-TUBE SPME-LC-MS/MS TO DETERMINE AMYLOID BETA PEPTIDES IN BIOLOGICAL SAMPLES OBTAINED FROM
PATIENTS WITH ALZHEIMER'S DISEASE

Caroline Fernandes Grecco*, Maria Eugênia Costa Queiroz

POSTER SESSION II: EuChemS-DAC Sample Preparation

Wednesday, 30 June 2021 (13:05-14:00/17:50:18:30)
Friday, 2 July 2021 (13:00-14:00)

P35 **DEVELOPMENT AND VALIDATION OF ANALYTICAL METHOD BASED ON MINIATURIZED MATRIX SOLID-PHASE DISPERSION FOR DETERMINATION OF PHTHALATES (PHTS) IN MUSSEL**
N. Carro*, J. Cobas, I. García, M. Ignacio, A. Mouteira

P36 **MULTI-RESIDUAL APPROACH FOR THE DETERMINATION OF BPA AND ITS SUBSTITUTES IN WATER AND SOFT DRINKS**
C. Fernández-Ramos, L. Herrero, L. Ramos, B. Gómara*

P37 **CLASSIFICATION OF OLIVE OIL QUALITY AND GEOGRAPHICAL ORIGIN BY USING A MULTI-CUMULATIVE TRAPPING HS-SPME-GC-MS FOLLOW BY A NOVEL DATA HANDLING SOFTWARE**
N. Spadafora, S. Mascrez, L. McGregor, G. Purcaro*

P38 **VOLATILE MASS SPECTRAL FINGERPRINTING BY SPME MS FOR CLASSIFICATION OF HONEY BOTANICAL SOURCE**
J.E. Quintanilla-López, R. Lebrón-Aguilar, A.C. Soria*

P39 **MOLECULARLY IMPRINTED POLYMER-HOLLOW FIBER MICROEXTRACTION OF HYDROPHILIC FLUOROQUINOLONE ANTIBIOTICS IN ENVIRONMENTAL WATERS AND URINE SAMPLES**
F. Barahona, B. Albero, J.L. Tadeo, A. Martín-Esteban*

P40 **EVALUATION OF 2-HYDROXYETHYL METHACRYLATE AS CO-MONOMER IN THE PREPARATION OF WATER-COMPATIBLE MOLECULARLY IMPRINTED POLYMERS FOR THE EXTRACTION OF TRIAZINIC HERBICIDES**
Esther Turiel, Antonio Martín-Esteban*

P41 **DETERMINATION OF ZINC OXIDE NANOPARTICLES IN MOSTURIZING CREAMS BY SP-ICP-MS**
Iria Rujido-Santos, Paloma Herbello-Hermelo, María del Carmen Barciela-Alonso, Pilar Bermejo-Barrera, Antonio Moreda-Piñeiro*

P42 **EXPLOITING 3D PRINTED DEVICES MODIFIED WITH CORE-SHELL MOLECULARLY IMPRINTED POLYMERS BASED ON METAL ORGANIC FRAMEWORKS AS ON-LINE EXTRACTION MICROCOLUMNS FOR AUTOMATIC DETERMINATION OF BISPHENOLS IN SEAWATER**
Enrique Javier Carrasco-Correa*, Ernest Simó-Ramirez, María Jesús Lerma-García, Ernesto Francisco Simó-Alfonso, Montserrat R. Delgado, Manuel Miró

P43 LOW COST 3D PRINTED SPECTROPHOTOMETER FOR SUNSET YELLOW AND TARTRAZINE SIMULTANEOUS DETERMINATION

Ezequiel Vidal*, Damián Uriarte, Sergio Pasini, Lorena Vidal, Mariano Garrido, Claudia Domini

POSTER SESSION III: General-Young

Thursday, 1 July 2021 (13:00-14:00)
Friday, 2 July 2021 (13:00-14:00)

P44 **DEVELOPMENT OF METHODOLOGIES TO OBTAIN BIOACTIVE PEPTIDES FROM POMEGRANATE SEEDS USING HIGH INTENSITY FOCUSED ULTRASOUNDS AND PRESSURIZED LIQUIDS**
Miriam Guzmán-Lorite*, María Luisa Marina, María Concepción García

P45 **SUITABILITY OF NATURAL DEEP EUTECTIC SOLVENTS IN COMBINATION WITH HIGH INTENSITY FOCUSED ULTRASOUNDS FOR THE SUSTAINABLE EXTRACTION OF PROTEINS**
Miriam Guzmán-Lorite*, María Luisa Marina, María Concepción García

P46 **GREEN SOLVENTS FOR SUSTAINABLE RECOVERY OF HIGH ADDED-VALUE VANILLA COMPOUNDS FROM WASTEWATER**
Raquel Cañadas*, María González-Miquel, Emilio J. González, Ismael Díaz, Manuel Rodríguez

P47 **MESOSTRUCTURED SILICA FUNCTIONALIZED WITH ACID SULFONIC GROUPS AS SORBENT FOR DISPERSIVE SOLID PHASE EXTRACTION OF TROPANE ALKALOIDS FROM AROMATIC HERBS AND SPICES**
Lorena González-Gómez*, Judith Gañán, Sonia Morante-Zarcero, Damián Pérez-Quintanilla, Isabel Sierra

P48 **MULTI-RESIDUE DETERMINTION OF ACRYLAMIDE AND FURANIC ALDEHYDES IN INSECT-BASED FOODS USING FUNCTIONALIZED MESOSTRUCTURED SILICA FOR SAMPLE PREPARATION PRIOR LC-TQ-MS/MS ANALYSIS**
Lorena González-Gómez*, Sonia Morante-Zarcero, Damián Pérez-Quintanilla, Isabel Sierra

P49 **MESOPOROUS SILICA-COATED MAGNETIC NANOPARTICLES TO EXTRACT SIX OPIUM ALKALOIDS IN EDIBLE POPPY SEEDS PRIOR TO HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY ANALYSIS**
Gema Casado-Hidalgo*, Sonia Morante-Zarcero, Damián Pérez-Quintanilla, Isabel Sierra

P51 **IDENTIFICATION OF VOLATILE COMPOUNDS IN EPOXY AND ORGANOSOL COATING BY P&T GC-MS**
Patricia Vázquez Loureiro*, Raquel Sendón, J. Bustos, Perfecto Paseiro Losada, Ana Rodríguez-Bernaldo de Quirós

P52 **MIGRATION OF COMPONENTS FROM EPOXY CAN COATINGS AND ANALYSIS BY LIQUID CHROMATOGRAPHY**
Antía Lestido Cardama*, Raquel Sendón, Juana Bustos, Mª Teresa Nieto, Perfecto Paseiro Losada, Ana Rodríguez Bernaldo de Quirós

P53 **SPME-GC-MS ANALYSIS OF POTENTIAL VOLATILE MIGRANTS FROM EPOXY AND ORGANOSOL COATINGS USED IN METAL FOOD CANS**
Patricia Vázquez Loureiro*, Raquel Sendón, J. Bustos, Mª Isabel Santillana, Perfecto Paseiro Losada, Ana Rodríguez-Bernaldo de Quirós

P54 **NON-TARGETED ANALYSIS FOR THE IDENTIFICATION OF VOLATILE COMPOUNDS FROM A POLYESTER COATINGS BY GAS CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY**
Antía Lestido Cardama*, Patricia Vázquez Loureiro, Raquel Sendón, Juana Bustos, Perfecto Paseiro Losada, Ana Rodríguez Bernaldo de Quirós

P55 **AMINO-FUNCTIONALIZED SILICA FROM RICE STRAW: NITRATE ADSORPTION**
H. R. Robles-Jimarez*, L. Sanjuan-Navarro, N. Jornet-Martínez, C. Molins-Legua, P. Campins-Falcó

P56 **STUDY OF FILTER BASED EXTRACTION OF CARBON BLACK NANOPARTICLES BY USING AF4-DLS**
L. Sanjuan-Navarro*, Y. Moliner-Martínez, P. Campíns-Falcó

P57 **NANO-LIQUID CHROMATOGRAPHY: FROM LAB TO PORTABLE EQUIPMENT**
S. Cortés-Bautista*, R. Navarro-Utiel, P. Campins-Falcó

P58 **TESTING SAMPLE INTEGRITY AFTER DILUTION BY USING SEVERAL MINIATURIZED LIQUID CHROMATOGRAPHY TECHNIQUES**
Rocío Navarro-Utiel, Sergio Cortes-Bautista, Pilar Campíns-Falcó

P59 **CHARACTERIZATION OF DIETARY SUPPLEMENTS BY PORTABLE HIGH PERFORMANCE NANO-LIQUID CHROMATOGRAPHY**
Camila Fernanda Soto-Soto*, Rosa Herráez Hernández, Pilar Campíns-Falcó

P60 **APPLICATION OF ENZYMATIC ASSAYS FOR THE DETECTION OF CHEMICAL CONTAMINANTS IN FOOD: THE IMPORTANCE OF EXTRACTION AND SAMPLE TREATMENT**
Ereño Artabe A.*, Cunha-Silva H., Barranco A.

P61 **ENZYMATIC EXTRACTION FOR THE ANALYSIS OF SILVER NANOPARTICLES IN CULTIVATED MUSSELS**
J.J López-Mayán*, E. Peña-Vazquez, M. C. Barciela-Alonso, P. Bermejo-Barrera, A. Moreda-Piñeiro

P62 **OVERCOMING LIMITATIONS OF TRADITIONAL SPME FIBERS THROUGH NOVEL FABRICATION TO DETECT PAHS IN WATER AND BABY FORMULA IN THE PARTS-PER-TRILLION REGIME**
George H. Major*, Dhananjay I. Patel, Matthew R. Linford, Jason Herrington, David S. Bell

P63 **EXTENDING THE APPLICABILITY OF FULLY AUTOMATED HIGH-CAPACITY SORPTIVE EXTRACTION FOR GAS CHROMATOGRAPHY MASS SPECTROMETRY**
Rachael Szafnauer, Natasha D. Spadafora, Laura McGregor, Nick Bukowski

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Mohamad Subhi Sammani*, Sabrina Clavijo, Andreu Figuerola, Víctor Cerdà

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P148 **ASSESSMENT OF HONEY AUTHENTICITY BY ANALYSIS OF AROMA VOLATILES USING HIGH-CAPACITY SORPTIVE EXTRACTION (HISORB) AND GAS CHROMATOGRAPHY – MASS SPECTROMETRY**
Natasha D. Spadafora*, Rachael Szafnauer, Rebecca Cole, Laura McGregor, Nick Bukowski

P149 DISPERSIVE SOLID-PHASE EXTRACTION USING MAGNETIC CARBON NANOTUBE COMPOSITE FOR THE DETERMINATION OF EMERGING MYCOTOXINS IN HUMAN URINE
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P151 MULTI-RESIDUE DETERMINATION OF EMERGING POLLUTANTS IN MUSSEL (MYTILUS GALLOPROVINCIALIS)
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SPME DEVICE DESIGN AND METHOD OPTIMIZATION USING FUNDAMENTALS

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The development of matrix compatible coatings for solid phase microextraction (SPME) has enabled direct extraction of analytes from complex sample matrices, including live tissue. The direct immersion (DI) mode of SPME when utilized in conjunction with such extraction phases facilitates clean extraction of a wide range of analytes from complex matrices without the occurrence of fouling or coating saturation as well as elimination of matrix effects when combined with LC/MS. In this presentation, mathematical models and computational simulations based on COMSOL combined with experimental validation were employed to investigate the effect of binding components present in complex samples on the recovery of metabolites varying in logP for extractions carried out using the direct extraction approach. The presented findings corroborate that the studied approach indeed enables the extraction of both polar and nonpolar analytes from complex matrices, provided a suitable sorbent is employed, so the technique is not only suitable for targeted determinations, but also metabolomics investigations. Further, results indicated that in certain cases, the kinetics of extraction of a given analyte through its free form might be dependent on the desorption kinetics of their bound form from matrix components, which might lower total recoveries of analytes with high affinity for the matrix. However, the binding of analytes to matrix components also enables SPME to extract a balanced quantity of different logP analytes, facilitated by multiphase equilibria in matrix, with a single extraction device. Experimental validation of this modeling approach was applied to understand the mass transfer of doxorubicin, anticancer drug, in lung tissue. This approach facilitated quantitative determination of the binding constant and diffusion coefficient. The developed computational model was also employed to elucidate practical aspects of different SPME geometries, in particular effect of miniaturization of SPME devices on the kinetics and efficiency of extraction. Particular focus was placed on fibers, tips and particle geometries of different size as they are more compatible with in-vivo extraction. The attained simulation results associated with the shape dependency on equilibration time were in good agreement with experimental observations, demonstrating that the mass-transfer limitation is highly dependent on size, shape and composition of the coatings. Higher enrichment factors are achievable with the use of a thinner coatings or fewer number of particles in comparison to factors achieved via exhaustive extraction. Composition of the coating is critical to obtain optimal performance.

ECO-EFFICIENT ANALYTICAL METHODOLOGIES USING ROTATING-DISK SORPTIVE EXTRACTION

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Rotating-disk sorptive extraction (RDSE) is an equilibrium-based microextraction technique which consists of the extraction of selected analytes onto a magnetic rotating Teflon disk coated with a sorbent phase [1]. The main advantage of this technique is the high mass transfer between the phases, which is achieved by the ability to reach high rotational velocities without tearing the extraction device. In addition, the great versatility of RDSE in the study of hydrophobic and hydrophilic analytes is evidenced considering the ease of immobilization of different sorptive phases in both laminar and particulate forms. The fundamentals, chemistries, and applications of RDSE have been recently reviewed [2].

In this work, we present three RDSE strategies developed in our laboratory: (a) spectroscopic direct measurements, (b) biomimetic method development and (c) use of natural sorptive phases.

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ELECTROMEMBRANE EXTRACTION – WHAT IS NEXT?

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With electromembrane extraction (EME), ionic analytes are extracted from aqueous sample, through a supported liquid membrane (SLM), and into a µL-volume of aqueous solution (acceptor). The driving force for the extraction is an external electrical field sustained over the SLM. The SLM is a µL-volume of an organic solvent, immiscible with water, immobilized in the pores of a solid membrane. The SLM separates the sample and the acceptor, and is compatible with complex biological and environmental samples. The acceptor is pure water with acid, base, or buffer. For extraction of basic analytes (cations), the negative electrode is placed in the acceptor, and the positive electrode is in the sample. Both the sample and the acceptor are kept neutral or acidic, to maintain the target substances positively charged. For extraction of acidic analytes, the polarity of the electrical field is reversed and pH is neutral or alkaline. Extraction selectivity is controlled by the chemical composition of the SLM, the direction and magnitude of the electrical potential, and pH in the sample and acceptor. Most matrix components of complex real samples are not extracted into the acceptor, and therefore EME provides a high level of sample cleanup. Since volumes of acceptor typically are 10-25 µL, EME provides pre-concentration. Acceptors are aqueous, and can be injected directly into LC-MS and related instrumental methods. EME can be conducted in 96-well format and in microchip systems, and commercial equipment is very close to market. The consumption of organic solvent per sample is less than 10 µL, and EME is therefore a green approach to sample preparation.

EME is an active field of research. This includes development of technical devices, new applications, and fundamental investigations about extraction principles. This presentation will introduce the principles of EME, discuss current research, and look into the future.

VACUUM-ASSISTED HEADSPACE MICROEXTRACTION: FASTER, BETTER, EASIER, GENTLER

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Vacuum is an emerging experimental parameter to control and exploit during headspace microextraction method optimization. The positive effect of vacuum was initially reported for headspace solid-phase microextraction (Vac-HS-SPME) sampling and resulting methods always used shorter extraction times and lower sampling temperatures compared to sampling under atmospheric pressure [1].

In this contribution the clear benefits of adopting the vacuum approach are presented through the discussion of several new applications from different collaborations. Initially, a new Vac-HSSPME method for the analysis of fish samples is discussed. The results showed that Vac-HS-SPME sampling under vacuum at 5°C yielded similar extraction efficiencies to those obtained with standard HS-SPME at 40°C. This is the first time that such a high sensitivity can be achieved at such a low sampling temperature, opening the door to new applications for the quality control of perishable foods.

Sampling under vacuum was found particularly beneficial not only for SPME but also for headspace microextraction methods using higher capacity extracting phases. An overview of the results and underlying mechanisms with vacuum-assisted headspace single-drop microextraction, vacuum-assisted headspace sorptive extraction (Twisters) [3] and newly introduced thin film microextraction (TFME) is given. The analysis demonstrates the pressure dependence of the underlying processes and predicts the superior performance of each method when sampling under vacuum. Finally, the commercialization of the vial closure that guarantees gastight conditions for extended times, fully compatible with any commercial multi-purpose autosampler is presented.

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STUDY ON IN VIVO SOLID-PHASE MICROEXTRACTION

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The development of techniques for monitoring analytes of interest in living systems is currently an important research topic. One of the main reasons behind is that in vitro techniques may not be able to accurately reveal the processes occurring in complex living systems. The application of solid-phase microextraction (SPME) in in vivo sampling can eliminate the errors, reduce the time associated with sample transport and storage, result in more accurate, precise, and faster analytical data, and therefore give a better indication of what will happen in the real world. Meanwhile, in vivo SPME permits repeated temporal and longitudinal studies.

In our group, research progresses have been made to ensure the accuracy, improve the sensitivity and promote the application of in vivo SPME. First, the difference of the mass transfer between the semi-solid samples and the fluid samples were illustrated, as well as the impact of the bound analyte on extraction kinetics. As a result, the basic theory for quantitative analysis was substantially improved.[1,2] Secondly, a serial of SPME coatings including the electrospun fibrous and etc. were developed.[3,4] The new coatings greatly increased the efficiency of in vivo SPME, and promoted the application of SPME in environmental analysis. Thirdly, new convenient, economical and green strategies were successfully developed for revealing the bioconcentration properties of pollutants.[5,6]

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ZEOLITES AND ZEOLITE-BASED MATERIALS: “OLD” MATERIALS FOR NEW APPLICATIONS IN SAMPLE PREPARATION

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The use of new solid materials as well as "old" materials rarely used as sorbents in (micro)extraction techniques is a very active research topic in chemical analysis. However, as of today, it can still be stated that zeolites and zeolite-based materials have been scarcely used as sorbents in (micro)extraction techniques. Promising new methods to determine organic and inorganic analytes based on these interesting materials have been developed. In addition, (micro)extraction methodologies based on the use of zeolites decorated with surface-modified magnetic nanoparticles with various functional groups or coating them with thin liquid films will be presented, which has allowed to synergistically combine the ease of handling with the improvement in the efficiency of sorption and selectivity of determinations. Due to the natural origin of the sorbent, the methodologies developed possess a strong environmentally friendly character.

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HEADSPACE SOLID PHASE MICROEXTRACTION APPLIED TO ANALYSIS OF COMPOUNDS WITH LOW VOLATILITY

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Solid Phase Microextraction (SPME), either using commercially available devices such as fibers or lab-made systems probably is the most popular extraction and pre-concentration technique applied to chromatographic analysis. When GC is used, the coupling with SPME is simple, fast and reliable particularly using headspace analysis (HS-SPME). However, there is a practical restriction on HS-SPME: it is limited to compounds with enough volatility to provide a minimum concentration on the vapor phase to allow their transport to the SPME fiber (species with boiling points up to 250 °C or vapor pressures of >10 Pa at ambient conditions). For solid matrixes, GC analysis of non volatile, non-derivatizable substances is usually carried out using lengthy and cumbersome procedures such as Soxhlet extraction – which demands usually aditional extract clean-up. Here, we will assess the combination of HS-SPME to two different approaches to allow its use on GC analysis of compounds with very low vapour pressures (10^{-7} bar or less): vaccuum-assisted Headspace SPME (Vac-HSSPME, firstly described by Psilakis and co-workers [1]) and Subcritical Water Extraction combined to SPME (SWE-SPME [2]). Both combinations where tested using apropriate samples (rock samples collected from stratigraphic exploratory oil wells), allowing better sensitivities and quantitative performance when compared to the traditional Soxhlet procedures.

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MICRODROP LIQUID-PHASE MICROEXTRACTION (SINGLE-DROP MICROEXTRACTION): COMING FULL CIRCLE?

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The introduction of solventless solid-phase microextraction (SPME) took place more than thirty years ago. Many have considered it to be a forerunner in the development of environmentally friendly sample preparation procedures. However, one can argue the trend actually began 15 years earlier when the solid-phase extraction cartridge was commercialized. Be that as it may, we were amongst the first to develop and report solvent-minimized extraction methods in which only low microliter volumes of organic solvent were consumed, in the mid-to-late 1990s. We referred to it then as liquid-phase microextraction (LPME) so as to be in descriptive symmetry with SPME. Soon after, this drop-based LPME approach became known as single-drop microextraction (SDME), and was widely applied. It was probably most extensively used in the first few years of its introduction, as expected of a new trend, before researchers began to move on to other configurations of microextraction (which continues to this day). Some 25 years later, SDME has come full circle: In the early 2000s, we have continued to devise applications for SDME. In this talk, we will present some of this work. We would like to think that the circle is not quite full yet, however, and there is yet more to expect from SDME, if researchers are creative!

SIMPLICITY, SUSTAINABILITY, AND SYNERGY: THE 3-S COMMITMENT OF CELLULOSIC SUPPORTS TO SAMPLE PREPARATION

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Advances in sample preparation include the use of novel solid and liquid phases usually immobilized on/confined by a solid support. In addition to their analytical performance, the potential of these approaches to be transferred to/reproduced by other laboratories or research groups must be taking into consideration when a novel sample treatment methodology is designed. The 3-S rule: *simplicity* of the synthesis, *sustainability* of the devices and *synergic* combination of the materials employed, would help to evaluate, and facilitate transferability. In our research group, the (ligno)cellulosic supports have been identified as a paradigmatic example.

As a support, paper allows the fabrication of cost-effective and disposable units that can be applied in planar microextraction formats. Cellulose fibers can interact with the target analytes through polar and cation exchange mechanisms. Additionally, its surface can be modified with a polymeric, nanostructured, or composite layer by dip-coating or covalent binding. Moreover, the final geometry can be easily adapted (simply cutting) to the extraction unit to be used for the extraction or even be used for the direct combination with the instrumental technique.

This communication presents our last contributions in the development of paper-based extraction units. Polymeric coatings of variable polarity have been deposited by dip-coating, while polymeric ionic liquids have been chemically bonded to the paper surface to improve its mechanical stability. Other coatings have been synthesized using carbon nanohorns, taking advantage of their nanostructured dahlia aggregates. Finally, the synergic combination of a polymeric phase with nanomaterials will be briefly described as well as their application to the photocatalytic degradation of priority pollutants or their use as substrates for surface enhancement Raman spectroscopy.

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DIFFERENT ANALYTICAL APPROACHES FOR EVALUATING THE ENVIRONMENTAL AND HEALTH IMPACTS OF RECYCLED CRUMB RUBBER USED IN RECREATIONAL AND SPORTS SURFACES

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In many developed countries, most discarded tires are mechanically transformed in crumb rubber for recycling. This product is mainly employed to build pavement surfaces of playgrounds and athletic courts, and as infill in synthetic turf of recreational and sports fields. Nevertheless, recycled crumb rubber is rich in compounds with recognized toxic potential including PAHs, plasticizers, antioxidants and vulcanizing agents, some of them considered carcinogenic and Substances of Very High Concern (SVHC) by the EU and international agencies. The investigation of these chemicals in the sports and leisure facilities, as well as in the surrounding environmental compartments, is of great interest to establish a diagnosis about the environmental and health impacts. In this project, different analytical strategies have been developed to monitor the crumb rubber used in playgrounds and football fields, stressing the high levels of toxic and hazardous compounds in both indoor and outdoor spaces [1,2]. A global study was carried out analysing real samples taken in more than fifteen countries and four continents, demonstrating the globalization of this problem. Analytical methodologies for the determination of these contaminants in water and air in contact with these surfaces have been developed. These methods based on miniaturized SPE combined with ultrasound extraction and SPME followed by GC-MS/MS analysis, showed the transfer of many contaminants from the surfaces towards the environmental matrices [2,3]. In addition, first experiments intended to evaluate the oral bioaccesibility are being carried out. In this case, a green method based on end-over-end extraction followed by mini-SPE is proposed.

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HIGH THROUGHPUT NUCLEIC ACID SAMPLE PREPARATION AND ANALYSIS

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Ionic liquids (ILs) can be designed to exhibit unique properties for their use in a number of applications in analytical and bioanalytical chemistry. This talk will focus on the design and synthesis of ILs, magnetic ionic liquids (MILs), and polymeric ionic liquids (PILs) as well as the use of these materials in a number of applications for the analysis of nucleic acids. Nucleic acids are biopolymers that constitute important diagnostic molecules for a broad range of applications from clinical testing to forensic analysis. A major challenge faced by DNA and RNA analysis techniques is the selective extraction of particular nucleic acid sequences using rapid and sensitive methodologies. It will be shown that ion-tagged oligonucleotides (ITOs) can be used in conjunction with MILs to efficiently capture DNA sequences from complex samples. The ITOs can be created through thio-lene "click" chemistry and the nature of the ion tag can influence the partitioning of the ITO to the hydrophobic MIL. This novel liquid-phase approach towards sequence-selective DNA capture provides superior extraction efficiencies to conventional magnetic bead technology as well as a platform for using external fields to manipulate the liquid droplets. The development of isothermal amplification approaches capable of achieving single-nucleotide resolution of nucleic acid sequences will be demonstrated through the use of molecular beacons.

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SPME-BASED SAMPLE PREPARATION STRATEGIES IN CLINICAL AND BIOMEDICAL ANALYSIS

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Solid phase microextraction is already well established method in bioanalysis, particularly for biofluid analysis. In the past few years it gained more interest as a low invasive tissue sampling method, also known as chemical biopsy. The unique features of the method, like small size of the probe, no physical consumption of tissue sample during extraction, solvent-free extraction and flexibility of experimental design due to the versatility of the sampling device geometries makes this technology very promising for clinical application on-site.

The current study presents the use of several different SPME sampling devices for in vivo and ex vivo analysis of drugs and endogenous substances (metabolites) in various tissues and biological fluids. The major challenge associated with in vivo studies is very short time of extraction, which compromises analytes recovery thus sensitivity and analyte coverage. To address this issue new sampling device made of a set of fibers was tested for the spatially resolved profiling of different brain regions. For the brain tumor study, traditional bioSPME fiber was used for the comprehensive investigation of glioma phenotypes. The data was compared with histological and genetic tests revealing compounds of potential use in diagnostic of this cancer. In addition, optimized analytical conditions along with the correlation with immunohistochemical study were applied in analysis of the level of endocannabinoids in selected brain structures. Moreover, SPME approach was employed to analyze the serum metabolome of patients with psoriasis, psoriatic arthtritis, and healthy controls in order to examine potential differences in the biochemical profiles at a metabolite level.

As the ultimate goal of biomedical SPME research is to propose solution for rapid on-site analysis, the proof-of-concept experiments involving direct coupling of Coated Blade Spray to Mass Spectrometry was performed for analysis of brain tumor samples. The results showed a potential of the strategy in disease diagnosis and monitoring of applied therapy.

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BEAD INJECTION LAB-ON-VALVE AUTOMATION FOR AFFINITY BASED SEPARATIONS

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The bead injection concept comprises the injection and transport of particles inside a flow system. Sample treatment and/or analysis are implemented in lab-on-valve (LOV) devices, which present more potential and compatibility with real-world samples when compared to microfluidic devices, due to the mesofluidic scale of their engraved flow channels [1]. The bead injection approach provides a fresh portion of sorbent, avoiding carry-over effects between samples and sorbent fouling from matrix components. Moreover, automation of column assembly provides repeatable packing of sorbent, with strict control of the flow rates applied during analyte retention and elution steps, contributing to acceptable results with significant reduction of sorbent amount.

In this work, the automation of solid-phase extraction based on affinity separations will be exploited. The coupling of LOV with BI permits the establishment of immunoassays under different formats (e.g. sandwich and direct competitive ELISA and immunoaffinity chromatography), with real time monitoring of reaction(s) directly on the solid support surface. These methods require minimal operator intervention and short time-to-result intervals. They allow for a high surface-to-volume ratio, they require low amounts of sample, sorbent, and reagents, while preventing fouling phenomena. Several examples will be critically discussed, including the assessment of IgG capture in immobilized protein A through automated BI-LOV with in situ spectrophotometric quantification [2]. The miniaturization and automation of ELISA protocols will also be presented, as a significant reduction on time-to-result is attained (2 h to 5 min) for carbamazepine and IgG quantification [3, 4].

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CONSIDERATIONS AND FUTURE TRENDS ON PASSIVE MICROEXTRACTION TECHNIQUES

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Passive microextraction techniques have played an important role as modern approaches to sample preparation for the past thirty years. Some good examples are liquid-based microextraction techniques, such as dispersive liquid-liquid microextraction (DLLME), single drop microextraction (SDME) and hollow fibre liquid phase microextraction (HF-LPME). On the other hand, solid base microextraction techniques have also been proposed, namely solid phase microextraction (SPME), stir bar sorptive extraction (SBSE) and, in the last decade, bar adsorptive microextraction (BAµE) [1]. In general, the main characteristics of these technologies are the use of miniaturized devices, great simplification, easy handling, great reduction or absence of toxic organic solvents, the use of a small sample volume, selectivity and sensitivity enhancement for trace analysis, as well as compatibility to interface with common chromatographic and hyphenated systems [2]. However, none of these microextraction techniques present "universal applicability". If we consider the current technological

and environmental requirements, some aforementioned microextraction techniques have several limitations to be considered as real alternatives in the future, especially if routine work is involved. In this context, passive microextraction techniques must be developed in a much simpler way, easy to handle, comprehensive, allowing automation, low cost, and global sustainability [3,4]. In this contribution, some innovative advances will be discussed, as well as future trends on passive microextraction techniques, proposing simple concepts that present "universal usability", namely user-friendly, ecological and economical approaches for daily analytical work.

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MIGRATION OF (SEMI-)VOLATILE ORGANIC COMPOUNDS INTO FOOD SIMULANTS FROM PLASTIC FOOD CONTAINERS AND MOLDS

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Food packaging materials made of plastic are used to protect food against external pollution. Other products, such as flexible silicone molds, offer numerous practical advantages compared with traditional cooking practices and, in consequence, are increasingly demanded by consumers. Nevertheless, none of these products are completely inert [1,2]. Apart from monomers, different types of additives and stabilizers are frequently added to these plastics during polymerization to improve the properties and durability of the final materials. Current legislation on plastic materials and articles intended to come into contact with food [3] assigns specific migration limits to substances with potential to migrate into food at concentrations that may either endanger human health or promote an unacceptable change in food composition or deterioration in its organoleptic characteristics. However, many studies have repeatedly reported on the capability of other components, including decomposition, reaction and intermediate products, antioxidants, and other non-intentionally added substances (NIAS) to migrate from plastic containers and flexible silicone molds into foods and food simulants [1,2]. In addition, it should be highlighted that silicones for food contact applications are not regulated at the EU level. On the contrary, they are expected to be covered by corresponding European national legislations.

This communication summarizes the most relevant results concerning the migration of (semi-)volatile organic compounds from commercial polypropylene food containers exposed to food simulants selected according to current legislation [3], for 10 days at 40ºC to simulate a long period of usage [4]. Problems encountered when trying to apply an equivalent lixiviation approach to flexible silicone molds will also be discussed.

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POTENTIAL OF IMPRINTED POLYMERS FOR THE SELECTIVE EXTRACTION OF TARGET MOLECULES AND METAL IONS FROM COMPLEX SAMPLES

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The determination of compounds (organic molecules or inorganic compounds such as metal ions) at very low levels of concentration is still a real analytical challenge in various application fields. The evolution of the instrumentation in terms of separation and detection allows a significant improvement of sensitivity and analysis time. However, the analysis of ultra-traces present in complex matrices often requires a step of purification and preconcentration prior to the analysis. Therefore, extraction sorbents based on a molecular recognition mechanism can be developed and used for the selective extraction of target compounds and some structural analogs, thus rendering their quantitative analysis more reliable and sensitive. For this, molecularly imprinted polymers (MIPs) and ion imprinted polymers (IIPs) have already shown a high potential for the selective extraction of target analytes from complex matrices.

Different imprinted sorbents were synthesized and evaluated for their potential to selectively extract a target analyte but also structurally related compounds from various complex matrices (real water, soils or biological fluids...). The conditions of synthesis were adapted in order to generate specific cavities for the selective trapping of the analytes. Their potential for the selective trapping of organic compounds or metal ions from environmental matrices and biological fluids will be presented, thus highlighting the advantages and limitations of MIPs and IIPs in terms of use, stability, selectivity, capacity and on-line coupling with HPLC.

Most of the developments were achieved by introducing the MIP particles in disposable SPE cartridges. However, these selective tools are also particularly necessary when developing miniaturized devices due to the decrease in resolution resulting from the use of short length separation devices. In this context, totally miniaturized analytical systems were developed for the quantitative analysis of target molecules in complex samples. Miniaturized MIPs were prepared by *in-situ* synthesis of imprinted monoliths in capillaries (I.D. 100 µm). The repeatability of the synthesis was assessed. At last, these miniaturized selective sorbents were coupled on-line to nanoLC and even directly to UV for the determination of organic compounds in biological fluids.

NOVEL MATERIALS IN ANALYTICAL SAMPLE PREPARATION: WHERE ARE WE GOING?

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Sample preparation is still the bottleneck in the analytical procedure, normally involving tedious and time-consuming steps, particularly when (i) dealing with complex samples, (ii) intending the determination of target analytes present at trace-low concentration levels, and (iii) pursuing proper compatibility with the further instrument used as detection system. In this sense, the design and application of advanced functional materials with enhanced extraction and selectivity features together with safer toxicological profiles has been one of the most exploited research lines within analytical separation science in the recent years, and clearly in sample preparation. Among the broad variety of materials explored, it is important to highlight (1) ionic liquids (ILs) and their derivatives – including polymeric ILs (PILs), ILs-based surfactants, and magnetic ILs (MILs), characterized by their outstanding solvation ability, high thermal and chemical stability, and impressive tunability; and more recently (2) deep eutectic solvents (DESs) and their natural derivatives (NADESs), also showing adequate stability and tunability. Both families of materials, ILs and DESs can be also highlighted by their green features and even biodegradability in some cases.

Regarding solid materials as sorbents, crystalline coordination polymers have attracted attention as sorbents due to their high surface area derived from the outstanding porosity, with special mention to (3) metal-organic frameworks (MOFs) and (4) covalent organic frameworks (COFs).

The aim of this presentation is to give an overview on the use that ILs and derivatives, and MOFs, have been had in our research group as novel materials for both liquid-based and solid-based microextraction strategies within analytical sample preparation, paying attention to the most recent advances together with a critical outlook on where efforts should be shifted in the field.

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ANALYSIS OF MICROPLASTICS IN WATER: FOCUS ON SAMPLING, SAMPLE PREPARATION AND GREEN ANALYTICAL PROTOCOLS

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The sampling, sample preparation and analysis of microplastics (MPs) pollution in water is identified as one major problem the world is currently facing. MPs can be directly released to water or formed by the degradation of bigger plastics. Nowadays, it is estimated that annually between 4 and 12 million tonnes of plastic go into the seas and oceans with a forecast for them to outweigh the amount of fish in 2050. Based on the existing studies, the characterization of MPs in waters is still one of the remaining challenges because they can be easily confused with organic or other types of matter. Consequently, there is an urgent necessity to establish analytical protocols for MPs in water [1]. This presentation will focus in three specific aspects of MPs determination in water: sampling, sample preparation and greenness of the analytical protocol. Examples on current monitoring of MPs in channels of Saudi Arabia will be reported too. Sampling, Separation, and Clean-Up. The main difficulties in sampling are representativeness and integrity. MPs are not homogeneously distributed in the water column but depending on MPs characteristics (density, shape, size) and environmental variables (type of water, streams, waves). Thus, one identified gap is that MPs profiling will be highly conditioned by the sampling method and there is no consensus on it. Three approaches nets, sieves, or pumps are commonly used. Net-based sampling devices with different mesh sizes including bongo nets (>500 µm), manta nets (>300 µm), and plankton nets (>200 and >400 µm) to filtration of grab samples (0.45 µm) established that MP concentrations using net-based methods were ∼3 orders of magnitude less than those obtained by filtration of 1 L grab samples. Mesh size is a critical point that determines the minimum size and the number of MPs detected. Furthermore, synthetic fibers and particles (as nanoplastics) having dimensions <25 µm easily bypass these devices. One point that needs to be emphasized is that there is an absolute lack of standardized method or guidelines to sampling water for MPs. Particularly, the use of different mesh sizes makes it difficult to compare the available monitoring data. Green Analytical Chemistry examines analytical methods from the point of view of their toxicity to both the environment and humans. The aim is to reduce emissions to the environment, as much as possible, and to make these methods safer for analysts, without losing their efficiency [2]- This will be related to the 12 principles of green analytical chemistry such as direct analysis, minimal sample size, in-situ measurements avoiding derivatization and reduction of the energy costs. among others. As examples of the application of the analytical protocols reported in this presentation we will show examples of MPs determination in water of the channels and ponds that conduct residual water in two most important cities of Saudi Arabia, Riyadh and Al-Jubail. MPs showed an average of 3.2 items/L in Riyadh and 0.2 items/L in Al-Jubail showing a statistically significant difference between both cities. Sampling with a Turton Tow Net of 20 µm mesh, fibers were dominant in all sites (60%). MPs size was mainly distributed between 80 and 250 µm (60%), and their major colors were white (40%), red (25%) and blue (20%). Infrared spectral analysis revealed that most of the selected particles were identified as MPs of polypropylene and polyethylene (48.3%) [3].

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FABRICATION OF 6-PHENYLHEXYL SILANE DERIVATIZED, SPUTTERED SILICON SPME FIBERS

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Recently, we have developed a method for fabricating SPME fibers with greater extraction efficiency, less carry over, and less phase bleed compared to commercial counterparts using a form of physical vapor deposition (PVD), i.e., sputtering, in conjunction with chemical vapor deposition (CVD) [1], [2]. Note that sputtering is the most widely used method for depositing thin films in industry. These methods were used to deposit porous films of silicon onto silica fibers via sputtering, with a subsequent reaction with a C18 silane through a CVD process. Here, we report the fabrication of 6-phenylhexyl (6-PH) silane derivatized sputtered silicon solid phase microextraction (SPME) fibers. We repeat that the processes used to make these fibers are industrially viable. This study has involved sputtering silicon on fused silica fibers under a range of different conditions, including using different sputtering times, which produces different film thicknesses, and throw distances, which affects the film morphology. A 6-PH silane coating was surface reacted onto the sputtered films after the silicon deposition. This presentation will focus on the fabrication of these fibers and how the various parameters change the material deposition, allowing for a surface with tunable properties to be deposited. The fibers were treated with piranha solution to increase the number of silanol groups on the surface of the sputtered silicon prior to silanization. The fibers were analyzed using scanning electron microscopy (SEM), contact angle goniometry, spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS), and time of flight secondary ion mass spectrometry (ToF-SIMS). Of course, their most important characterization was their performance in SPME-GC.

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HOLISTIC BISPHENOLS ASSESSMENT BY SUPRAMOLECULAR SOLVENT-BASED SAMPLE TREATMENT PLATFORM

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Bisphenols are monomers used in the production of polycarbonates and epoxy resins. Many of these bisphenols, as well as their derivatives, have already been found in humans, wildlife, and the environment. These emerging compounds are suspect of presenting adverse effects in humans and animals through genomic and non-genomic pathways. The growing demand for a better understanding of the effects of chemical mixtures on human health has fostered the need to detect new exposure sources and achieve an extensive estimation of uptake rates from identified sources and/or biomonitoring. This research intends to develop an analyte- and matrix-independent analytical method for performing both the determination of bisphenols in multiple sources of exposure and biomonitoring studies. A comprehensive sample treatment platform for the simultaneous extraction of bisphenols from multiple human exposure sources and biological fluids based on the use of supramolecular solvents (SUPRAS) is proposed. Given the high variability of the matrices in terms of physical state (solid, liquid), composition (proteins, fats, fibers) and expected levels of bisphenols concentration (pg-mg), studies of selectivity and recovery were performed. Selectivity has been calculated as signal suppression or enhancement (SSE), getting values ranged 80-120%. Whilst a highly efficient extraction of bisphenols and derivatives was obtained for all the matrices, due to the mixed-mode mechanisms (hydrogen bonding, polar and dispersion interactions) and the huge number of binding sites offered by the SUPRAS for solute solubilization. The method was applied to the determination of bisphenols and derivatives in human exposure sources (beverages, canned-food, dust) and biological fluids (urine, serum, saliva). This analyte- and matrix-independent method constitutes a valuable strategy in terms of analytical and operational characteristics for the assessment of human exposure to mixtures of bisphenols and derivatives.

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PRE-SCREENING ASSAY BASED ON FAST BLUE B FUNCTIONALIZED SILICA-POLYMER COMPOSITE TO EVALUATE 3,5-DIHYDROXYHYDROCINNAMIC ACID AS BIOMARKER OF GLUTEN INTAKE

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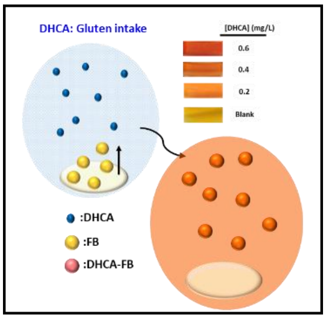
In the last years, there is an important need of precise biomarker(s) to assess dietary compliance of celiac patients given the relevance of this health problem in our society. Medical services and patients demand simple, rapid and in-situ devices that allow the estimation of these biomarkers in urine to obtain rapid responses to potential dietary transgressions.

Hence, in this work, a pre-screening colorimetric assay based on a silica–polymer composite doped with fast blue B reagent (FB) has been proposed to estimate 3,5-dihydroxyhydrocinnamic acid (DHCA) concentration in urine samples as potential biomarker of gluten intake. The proposed assay is based on the release of FB from the membrane to the DHCA solution to form the azo-derivative compound that can be detected by a change in the solution colour from pale yellow to reddish. Spectroscopic measurement at 520 nm and chromatographic measurements, using in-tube SPME-CapLC-DAD have been carried out to evaluate the responses. Sensitivity and precision were adequate for the DHCA estimation. LOD varied from 10 to 120 µg L^{-1}, depending on the volume of processed sample and RSD was up to 15%. Preliminary studies in urine samples displayed successful results, showing DHCA can be used as biomarker of gluten intake. The here proposed methodology clearly simplifies the dietary transgression evaluation thanks to the development of a pre-screening tool before the chromatographic analysis.



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CAPILLARY ELECTROPHORESIS FOR THE AUTOMATED EXTRACTION AND ANALYSIS OF DRIED BLOOD SPOTS IN CLINICAL ANALYSIS

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Traditional clinical assays require the presence of investigated subjects in clinical centres and use substantial volumes of blood. They are time-consuming for both the subjects and the clinical centres, moreover, blood withdrawals usually involve venous phlebotomy. Micro-sampling in the form of dried blood spot (DBS) has been presented as a viable tool for blood sampling, nevertheless, DBS micro-sampling suffers from several drawbacks, such as haematocrit effects, biased quantitative analyses and manual DBS extractions [1].

In the actual lecture, a novel all-in-one concept is presented that enables at-home self-sampling of exact blood volume (independent of blood haematocrit), DBS transport to the laboratory by mail and fully automated DBS extraction/analysis by capillary electrophoresis (CE) [2]. The proposed concept, therefore, significantly improves the life quality of the subjects (no venous phlebotomy, no visits to medical centres) and automates the DBS extraction and analysis (no manual handling of biohazardous materials by analysts). Moreover, it offers an elegant analytical tool for the actual pandemic situation, which requires considerably reduced personal contacts among the subjects and the clinicians but maintains the need for frequent and regular clinical blood testing.

As a proof-of-principle, the proposed concept was exemplified by the determination of warfarin, which requires frequent testing during the therapy, nevertheless, this concept can be extended to a wide range of other clinically relevant compounds. The presented concept is, therefore, of paramount significance since it provides a general solution to the personalized health monitoring, offers an analytical tool for clinical assays in critical situations, and might also propel a shift from the actual sick-care to a prevention-based healthcare system.

Acknowledgement

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ON-LINE SOLID-PHASE EXTRACTION CAPILLARY ELECTROPHORESIS-MASS SPECTROMETRY WITH A NANOLITER VALVE FOR THE ANALYSIS OF PEPTIDE BIOMARKERS

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On-line solid-phase extraction capillary electrophoresis-mass spectrometry (SPE-CE-MS) in the unidirectional configuration without valves is a very simple and low-cost technique for high throughput sample clean-up and analyte preconcentration, separation, detection and characterization [1]. However, in this configuration, the sample volumes introduced by pressure depend on the dimensions of the separation capillary and some matrix components can be irreversibly adsorbed in the inner capillary wall. Furthermore, in many cases, the requirements of the on-line extraction are incompatible with the background electrolyte necessary for an efficient separation and sensitive MS detection. Here, we present SPE-CE-MS with a nanoliter valve (nvSPE-CE-MS) to overcome these drawbacks while keeping the design simple [2]. The nvSPE-CE-MS system is operated with a single CE instrument and two capillaries for independent and orthogonal SPE preconcentration and CE separation, which are interfaced through an external and electrically isolated valve with a 20 nL sample loop. The instrumental setup is proved for the analysis of opioid and amyloid beta peptide biomarkers in standards and plasma samples, to fairly compare later the performance of nvSPE-CE-MS and unidirectional SPE-CE-MS.

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FIBREATHALYZER-4000 A USEFUL DEVICE FOR ANALYSIS OF COVID-19 IN EXHALED BREATH- AN ASCEDENT PROPOSAL

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The research is based on multi-MS platform strategy for covid-19 disease breathomics involving analytical flow path from exhaled VOC sampling, mass peak identification, compound assessment and statistical analysis. The main goal is to design a fast, low-cost, non-invasive tool/procedure for the early detection of Covid-19 in exhaled breath of patients by a metabolomic approach for the identification of biomarkers indicating the presence of the SARS-cov-2 virus using gas chromatography coupled to mass spectrometry after headspace fibreathalyzer-4000-GC-MS of the volatile organic compounds present in the samples collected. The specific objectives are the development and validation of the analytical methodologies using gas chromatography coupled to mass spectrometry after headspace fibreathalyzer-4000-GC-MS for the analysis of volatile organic compounds (VOCs) in exhaled breath of patients and controls for covid-19 [1-2]. To Identify specific biomarkers of the SARS-cov-2 virus in early stages of the disease in symptomatic, asymptomatic and control patients by multivariate analysis of breath VOCs and a metabolomic approach using bioinformatic platforms. The main task are: 1- VOC acquisition: this task implies the breath sampling and gas chromatography separation coupled to mass spectrometric detection with electron impact ionization as ionization mode GC-EI-MS. 2- VOC identification: this task implies in first step the data preprocessing trough peak alignment and baseline adjustment and in second step the peak annotation by using retention index RI for gas chromatography separations (GC); character fragments m/z for mass spectrometry detection in electro impact ionization mode EI-MS and molecular ion for mass spectrometry detection in other softer ionization mode APCI-MS. 3- VOC modelling: this task implies in first time the peak assessment in peak area for VOCs for gas chromatography coupled to mass spectrometry (GC-MS) and in the second time with all data the statistical analysis.

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AUTOMATED HIGH-THROUGHPUT MEASUREMENT OF PROTEIN BINDING USING SOLID PHASE MICROEXTRACTION AND LC-MS/MS

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The use of Solid Phase Microextraction (SPME) has been widely accepted as a fast and convenient sample preparation method. It has been applied to a wide range of samples and utilizes adsorbent-containing coated devices. Solid phase microextraction can be utilized in a highly throughput manner towards analysis of compounds in biological samples.

The use of a coating consisting of bio-compatible binder in combination with C18 adsorbent allowed extraction of small pharmaceutically relevant molecules. Protein binding is an important property of pharmaceutical compounds as only the free fraction exerts a pharmacological effect. Using a 96-pin BioSPME device allowed quantitative measurement of free fraction of pharmaceutical drugs from plasma using LC-MS/MS detection. The extraction method for the BioSPME device was developed on a Hamilton Starlet system. The obtained protein binding values for multiple pharmaceutical compounds were comparable to literature references. The results of the protein binding measurements will be presented for compounds across the range of hydrophobicities, charges, and molecular weights. The proposed sample preparation method provided high accuracy of the obtained protein binding values and was at minimum 3-times faster in comparison to the standard methodology. The extraction reproducibility for the BioSPME process was evaluated using extraction of multiple compounds with values within 15% RSD.

HS SPME-MS AS A TOOL FOR RAPID AUTHENTICITY AND QUALITY CONTROL OF ALCOHOLIC BEVERAGES

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Solid phase microextraction (SPME) gained extreme popularity in the analysis of food volatile compounds as extraction technique providing fiber coating related selectivity and high pre-concentration of samples from various matrices for their subsequent chromatographic analyses. In food analysis headspace (HS) SPME is usually performed. SPME can also be used for extraction of volatiles in quasi electronic noses based on mass spectrometry (HS SPME-MS). In this case volatiles extracted by SPME are desorbed with no separation into mass spectrometer and volatiles "averaged mass spectrum" is treated as a "sensor" response and subjected to MVA statistical analysis [1].

The presentation will focus on using HS-SPME-MS for two goals: sample classification and quality control based on presence of target compounds. The first approach will be discussed based on Baijiu spirits flavor and regional classification [2]. The second approach will be discussed based on monitoring of two compounds: *i)* 2,4,6-trichloroanisole (TCA) in wine, which is a main compound responsible for a "corky taint", and *ii)* geosmin in Baijiu spirits. Both compounds result in musty – earthy off-odors and their odor thresholds are usually in low ng/L depending on a matrix. Specificity of fast SPME sampling will be discussed, matrix effects, multiple extraction from a single vial, as well as analytical approaches using full scan data collection vs. selectivity provided by tandem mass spectrometry for compounds of interest analysis. Data treatment will be discussed as an important part of analytical procedure. Results of HS-SPME-MS will be compared to SPME with chromatographic separation for these applications.

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DISPERSIVE LIQUID-LIQUID MICROEXTRACTION COMBINED WITH PLASMA-BASED SPECTROMETRY DETECTION: PAST, PRESENT AND FUTURE

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Dispersive liquid-liquid micro-extraction (DLLME) has been stablished as a fast and green sample preparation methodology to improve figures of merit and reduce matrix effects from complex matrices. Though traditionally employed for the analysis of organic species, DLLME might be employed for elemental determinations by using a chelating agent to favor analyte extraction to the organic acceptor phase [1]. Analyte detection is usually accomplished by means atomic absorption spectrometry techniques due to the robustness of the atomization sources (flame or furnace) when dealing with organic matrices. To date, plasma-based techniques (i.e., microwave induced plasma optical emission spectrometry, MIP-OES, inductively coupled plasma optical emission spectrometry, ICP-OES, inductively coupled mass spectrometry, ICP-MS) have been scarcely employed in DLLME applications, despite their superior figures of merit and analytical performance (e.g. multielement determinations, sample throughput, etc.). The lack of applications is mainly derived by the limited plasma tolerance to organics and difficulties handling the limited volume available after the microextraction procedure [1]. In recent years, this research group has extensively investigated how to take advantage of such coupling for the development of new methodologies for the analysis of environmental and food samples. Our research efforts have been focused on: (i) the development of new chelating agents for metal extraction (i.e. task-specific ionic liquids); (ii) selection of sample introduction systems to efficiently low sample volumes; and (iii) mitigate spectral and non-spectral interferences due to organic extractants and sample matrix concomitants through the appropriate selection of plasma operating conditions and calibration strategies [2,3,4,5]. The aim of this work is to provide an overview of recent applications and current challenges in this field.

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O10

TOWARDS THE KNOWLEDGE OF NANOSCALE INTERACTIONS IN THE CONTEXT OF LIQUID CHROMATOGRAPHY: NEW OPPORTUNITIES FOR/FROM NANOSCALE AND LC

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Research is focused at generating new knowledge on the binomial nanoscale-liquid chromatography (LC). As tools, it uses new trends on analytical chemistry, sustainable chemistry, principles of miniaturized LC and its coupling on-line to IT-SPME and (nano)materials, an analysis of the background research and the environment and health as framework of actions. MINTOTA contributed to the aforementioned binomial [1-3], but more work is in progress (see Figure 1). It is intended to show the capabilities of IT-SPME-NanoLC for: characterization of nanoparticles and their dispersions, their behaviour in the fields of study, in following plasmonic assays particularly and also as a contribution to nanoparticles chromatography. Moreover, it is aimed to exploit the nanoscale for the implementation of new setups and phases for IT-SPME-NanoLC in order to improve its figures of merit, applications and sustainability, contributing to the nanoscale too. Portability is also discussed.

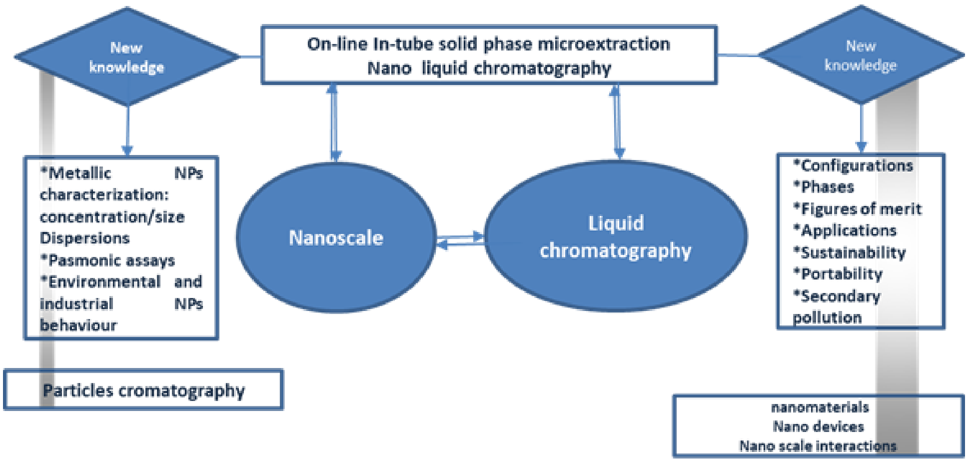

Figure 1. Some topics about the binomial: Nanoscale-Liquid Chromatography

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SAMPLE PREPARATION UNDER TURBULENT FLOW WITH RENEWABLE SORBENT

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Turbulent flow chromatography (TFC) is an SPE mode, presented some years ago as a universal sample preparation platform. It could perform concentration, matrix cleanup and medium exchange very fast, and additionally introduced a molecular weight cutoff so that high molecular weight interferences are excluded during the SPE loading step. This technique is however patented, and the expensive hardware, along with the shot lived consumables prevented its spread.

In this contribution we resort to the unconventional bead injection analysis for executing the TFC resorting to an inexpensive SPE bulk sorbent, a bidirectional pump, and a selection valve. Benefits include the reduced cost, the minimized use of reagents, samples and waste generation, the possibility to select the SPE chemistry at real time, and the unattended operation. Moreover, the flexible operation of the pump and valve setup is exploited to integrate other sample preparation operations.

An intelligent method has been developed as QC for the sorbent packing and the TFC performance has been exemplified with proteins as model interferences. A final proof of concept is presented where the Gd present in surface water is fractionated into free, complexed to low or high molecular weight compounds.

Acknowledgement

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CRITICAL EVALUATION (OPTIMISATION) OF ANALYTICAL EXTRACTION OF PLASTICISERS IN FOOTWEAR MATERIALS

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According to European Regulation [1-3] and the Consumer Product Safety Improvement Act, CPSIA [4], the content of twelve phthalates, which have been identified as substances of very high concern (SVHC), has been restricted and this list is expected to increase. Due to public health concerns about the presence of phthalates in consumer goods, the goal of this study was the optimisation of analytical extraction of phthalates in footwear materials using three factorial experimental design with two extraction techniques, microwave and ultrasonic techniques. In this work, the analytical extraction process was optimised by applying 3-level Factorial Design on one polymeric footwear sole sample. According to ISO 16181-1 [5], a mixture of hexane:acetone was employed in the extraction step by applying microwave and ultrasonic techniques, and the effect of 4 factors (temperature, solvent mixture, time, extraction volume) was studied in 81 runs. The third factorial experimental design was based on ISO 14389 [6], where tetrahydrofuran dissolved the polymeric content in the sample and then the dissolved polymer precipitated using the appropriate solvent (hexane or methanol); the optimised process was carried out by applying the 3-level factorial design, 3^3 (temperature, time, extraction volume) and the effect of 3 factors was studied in 27 runs for each solvent used in the precipitation step. The experiments were performed using Gas Chromatography/Mass Spectrometry (GC/MS) equipment. In each extract, the quantified plasticisers were 12 phthalates categorised as SVHC and other industrial plasticisers (terephthalate, adipates, citrates, and phosphate). The optimized conditions were validated for selectivity/specificity, precision, sensitivity (evaluation of LOD and LOQ), as well as for repeatability and matrix interference in a group of twenty footwear components. As a conclusion, the proposed analytical extraction method successfully quantified all plasticisers regardless of the molecular structure of the different footwear polymeric samples analysed.

Acknowledgements
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EXPLORING THE APPLICATION OF SELF-IMMOLATIVE POLYMERS IN SAMPLE PREPARATION

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Self-immolative polymers (SIPs) are macromolecules capable of disassembling in a domino type mechanism, “from head to tail”, when subjected to a suitable external stimulus [1]. The key factor of the immolation relies on the existence of a trigger group that can be activated by either a biological (enzyme, antibody, etc.), physical (temperature, light, etc.) or chemical (pH, solvent, salt, etc.) stimulus [2]. Having a good responsiveness and adaptability, these stimulus-sensitive polymers have been extensively studied and exploited in several fields, such as electronics, photonics, controlled drug administration, imaging and medical diagnosis [1]. However, to the best of our knowledge, they have not been applied in Analytical Chemistry, where they could play an important role in sample preparation. In particular, their capability of disassembling would provide an additional value when used as extraction sorbents, since such fact could facilitate their final degradation, minimizing environmental pollution, among other issues.

In this work, we will show our first results regarding the synthesis, characterization and application of a new SIP that was used as sorbent in dispersive solid-phase extraction (dSPE). After the design of the SIP, and once applied in dSPE, different stimulus were tested to try to initiate the disassembling mechanism in a simple and direct way in order to facility its later degradation process. These first results suggest that this relatively new type of polymers could be successfully used as “smart materials” for different sample preparation approaches.

Acknowledgement

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A SIMPLE METHODOLOGY BASED ON POLYMER INCLUSION MEMBRANES AND XRF ANALYSIS FOR THE MONITORING OF METALS IN NATURAL WATERS

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In this study, we present the use of a polymer inclusion membrane (PIM) to extract and preconcentrate metals from natural waters to facilitate their determination. In PIMs, a suitable extractant is immobilized within the chains of a plasticized thermoplastic polymer, such as cellulose triacetate (CTA). The polymer provides the membrane with mechanical strength, whereas the carrier is the responsible for the extraction. In general, PIMs are easy to prepare, possess good mechanical properties (e.g. strength and flexibility), and are versatile in terms of the target chemical species they can extract. In a recent work, we showed the efficiency of a PIM containing as a carrier the ionic liquid (IL) trioctylmethylammonium thiosalicylate (TOMATS) to extract Hg in water samples, and a methodology was developed based on the extraction and subsequent determination of the metal collected in the membrane by X-ray fluorescence spectrometry (XRF) [1].

In the present work, we have investigated two different carriers to be incorporated in a PIM: the commercial IL Cyphos IL 104, and the task-specific IL TOMATS. PIMs were prepared in a compositon 50%CTA-50% carrier(w/w) and were mounted in teflon holders to be used as monitoring devices. The sudy site was the Osor river, situated in North-East Catalonia (Spain), which is influenced by continuous (effluent) and diffuse (run-off) metal inputs from a disused mine. PIM-devices were deployed for 24 h, and, afterwards, they were directly analyzed by a low power benchtop Energy Dispersive XRF (EDXRF) spectrometer. This new methodology allowed the easy detection of both Zn and Cu in the river water.

Acknowledgement

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MOLECULARLY IMPRINTED POLYMERS FOR THE SELECTIVE EXTRACTION OF ENVIRONMENTAL CONTAMINANTS

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In this work, new MIPs have been synthesized as monodisperse microspheres for the selective extraction and preconcentration of different target contaminants: tetrabromobisphenol A (TBBPA), perfluoroalkyl substances (PFAS), nonylphenol and toxic elements (arsenic and methylmercury). MIPs are highly crosslinked and porous polymers that have been prepared in the presence of a template. After polymerisation the template is removed leaving specific recognition sites complementary to the template molecule. There are several variables affecting the recognition phenomena, but the nature of the interactions between templates and functional monomers is fundamental. Therefore, the selection of an appropriate composition of the pre-polymerization mixture (template, monomers, cross-linker and porogen) is very important to achieve the desirable characteristics of selectivity and affinity of the final MIP.

Suitable templates have been selected and after a deep *in silico* study the best polymerisation conditions were established. In the case of toxic elements, a specific chelating agent was required for the preparation of MIPs. In parallel to the fabrication of MIPs, non-imprinted polymers (NIP, polymer developed in the absence of the template) were also developed to study the imprinting effect.

The MIPs fabricated for PFAS showed the strongest affinity and have the highest number of active sites. Therefore, they were used to develop new methods. Regarding TBBPA and Nonylphenol, MIPs with lower affinity and lower number of active sites were achieved. However, affinity was observed and their use as material for sample preparation was assessed. In the case of arsenic and methylmercury, the NIP gave better response than the MIP. High affinity was observed but very low number of active sites were obtained.

In all cases small particles have been obtained (diameter below 1µm) which are also suitable for future sensor development.

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PARALLEL ARTIFICIAL LIQUID MEMBRANE EXTRACTION OF ORGANOPHOSPHORUS NERVE AGENT DEGRADATION PRODUCTS FROM ENVIRONMENTAL SAMPLES

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Alkyl methylphosphonic acids (AMPAs) are important environmental markers of nerve agents. Their analysis is still challenging because of their very polar and acidic character. Indeed, a sample pretreatment is needed before their separation in order to extract and preconcentrate them from complex samples. An emerging miniaturized high-throughput microextraction technique named “Parallel artificial liquid membrane extraction (PALME)”[1] coupled with liquid chromatography–tandem mass spectrometry was, for the first time, investigated for the extraction and enrichment of the AMPAs from environmental samples. The effect of various extraction parameters (nature of the membrane, the extraction solvent, the pH values of both donor and acceptor phases, agitation speed and extraction time) was studied in pure media (spiked deionized water samples). The impact of temperature and ionic strength on extraction efficiency was also investigated for the first time. The resulting optimized conditions were applied to environmental samples (river water, simulated waste water and aqueous soil extracts) to evaluate the performance of the method in terms of efficiency and repeatability in these real media. The developed method led to an almost exhaustive extraction for 4 of the 5 targeted AMPAs from pure water and to high enrichment factor (42.4 for the less polar compound). The major limitation of PALME regarding the low enrichment factors was overcome in this study thanks to the new set up of experiments. A detailed comparison between the results previously obtained with hollow fiber liquid-phase microextraction (HF-LPME) [2][3] and PALME for the extraction of AMPAs demonstrated the ease of transfer of method from HF-LPME to PALME which could lead to an easier development of PALME for many compounds from the large amount of HF-LMPE data available in the literature.

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AN EASY-TO-PERFORM ANALYTICAL METHOD FOR THE DETERMINATION OF IBUPROFEN AND ITS MAIN METABOLITES IN MARINE BIVALVES

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It is well-known that pharmaceuticals are continuously released to the aquatic environment but their presence in the marine environment and in aquatic organisms has been scarcely evaluated to the date [1,2]. In addition, metabolites of pharmaceutical compounds, which can be more toxic and present in the aquatic environment at higher concentrations than their parent compounds [2], are even more rarely monitored in aquatic organisms. This fact is of special relevance in marine edible organism such as some bivalves. In this work, a low-cost and easy-to-perform analytical method has been developed and validated for the first-time determination of ibuprofen and its metabolites in mussels. The method is based on ultrasound-assisted extraction, with methanol containing formic acid 0.5%, v/v, extract clean-up by dispersive solid-phase extraction with C18 and Florisil and analytical determination by liquid chromatography-tandem mass spectrometry. A Box-Behnken experimental design was applied to sample treatment optimization to reduce the number of experiments and to better evaluate the influence of the different variables. The method was validated using mussel *Mytilus galloprovincialis*. Extraction recoveries were in the range from 81% to 115%. Inter-day precision was lower than 7%. Method detection limits were in the range from 0.1 to 1.9 ng g^{-1} dry weight.

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VOLATILE METHYL SILOXANES IN WASTEWATER TREATMENT PLANTS: ANALYSIS AND QUANTIFICATION

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Wastewater treatment plants (WWTPs) are, at the same time, important sinks and sources of volatile methylsiloxanes (VMSs) [1]. These chemicals of emerging concern (CECs) are extensively produced and used in numerous industrial processes and consumer goods such as personal care products (PCPs). Reaching WWTPs mainly through wash-off of PCPs and industrial effluents, they tend to partition to the sludge given their lipophilic nature and be released to the atmosphere due to their volatility. In WWTPs, among other potential hazards, they can hamper the use of biogas as a renewable fuel for the production of energy (*e.g.* cogeneration) [2] and may be a risk to the workers via dermal contact or inhalation exposure. In such a dynamic environment, the study of siloxanes is complex and requires comprehensive mass balances that take into account all the main matrices involved: wastewater, sludge (liquid and solid), air and biogas. One of Project LANSILOT's tasks is to face this challenge resorting to analytical protocols in line with the "Green Analytical Chemistry" principles. This work describes the optimization of methods to extract and quantify seven VMSs (L3, L4, L5, D3, D4, D5, D6) in the aforementioned target matrices and shows the first results of the initial sampling campaign in a WWTP to assess their levels, distribution and trends throughout the treatment steps.

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NEEDLE TRAP MICRO EXTRACTION (NTME) – A COMBINED POC SAMPLING & PRE-CONCENTRATION TECHNIQUE FOR VOC PROFILES IN BIOMEDICAL ANALYSIS

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The analysis of volatile organic compounds (VOCs) represents an innovative scientific approach in bio-analytical chemistry. As a quick and completely non-invasive analytical technique, several biomedical research approaches promise new insights into physiology and pathophysiology *in vitro* and *in vivo* [1]. As biogenic VOCs occur in very low concentrations (pmol/L-nmol/L) and may easily be affected by sampling, storage or decomposition, a well-established method for PoC sampling and pre-concentration is crucial for successful studies. Microextraction techniques such as needle trap microextraction (NTME) fulfill these requirements. Needle trap devices (NTDs) have shown many advantages such as improved reproducibility, low limits of detection, limits of quantitation and carry over as well as excellent storage properties if compared with established techniques in VOC analysis such as SPE or SPME.

The analytical performance of NTME highly depends on sorbent materials, desorption temperatures and applied sampling conditions. Even small fluctuations in material and performance make trace analysis difficult. To ensure efficient sampling of volatiles and avoid e.g., breakthrough or memory effects it is necessary to adapt materials and sampling procedures to physiochemical VOC properties, perform intensive inspection and testing and introduce a standardization process. Done properly NTME provides excellent results for the detection of VOC profiles down to pptV range [2].

In this presentation advantages and drawbacks of NTME as well as results of various *in vitro* and *in vivo* studies using NTME will be discussed.

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A NEW APPROACH TO FAT DETERMINATION IN FOOD AND FEED SAMPLES USING MICROWAVE ASSISTED EXTRACTION

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Total fat determination in food and feed matrices is a routine analysis for several testing and food processor labs, as it is part of labelling process and QC testing. In QC and food testing laboratories a single method approach and high throughput are valuable factors to streamline the lab workflow. Nowadays, the process still relies on outdated and matrix-dependent methods which use obsolete and time-consuming technologies. The microwave extraction method enables simultaneous hydrolysis and extraction in less time, ensuring higher productivity and better workflow. The new method for total fat determination is not matrix dependent, therefore, it uses a single method and setup for virtually any sample and total fat contents. The proposed approach offers the ability to process 45 samples in a single working day, ensuring lower cost per sample and offering complete fat determination. Traditional extraction techniques are based on the Soxhlet technique, which uses elevated acid and solvent volumes for the hydrolysis and extraction steps, respectively. The ETHOS X's closed-vessel technology offers a substantial reagent and waste reduction. While Soxhlet and automated Soxhlet systems demand around 100/ 200 mL of reagents per sample, the ETHOS X only requires 35 mL. The low reagent consumption in combination with the higher productivity and competitive initial investment offers lower cost per sample.

NEW MOBILITY DIMENSION FOR THE ANALYSIS OF PRIORITY HAZARDOUS SUBSTANCES IN WATER BY TISMTOF

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In this presentation, we will show the latest results using the state of the art timsTOF high resolution mass spectrometry system, with the trapped ion mobility dimension, for a truly 4D screening analysis of priority pollutants in water. The measurement of the CCS values, in the tims TOF system, enables rapid discrimination of the complex PFOAS isomers mixtures, improving sensitivity and analysis time. This family of priority pollutants is of growing interest, and usually a very complex analytical challenge for the usual techniques including high-resolution mass spectrometry approaches. Here the extra dimension of trapped ion mobility plays a key role.

USING ACCELERATED SOLVENT EXTRACTION TO UNCOVER SUBSTANCES OF TOXICOLOGICAL INTEREST IN BONES AND BLOOD SAMPLES

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In forensic contexts of advanced decomposition, when conventional matrices are no longer available for toxicological analyses, finding alternative matrices is necessary.

The skeleton, which is fundamental for anthropologists and geneticists, could be useful also for toxicological purposes to help establish a cause of death. What kind of information can be gained from toxicological analysis performed on bones (the cranium and the ribs) in different states of preservation? This presentation will show how accelerated solvent extraction was used to extract drugs of forensic interest before being analysed on with high performance liquid chromatography coupled to a high-resolution mass spectrometer.

NATURAL PRODUCT PREPARATIVE SEPARATIONS BY CENTRIFUGAL PARTITION CHROMATOGRAPHY (CPC)

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Centrifugal Partition Chromatography (CPC) also known as Countercurrent Separation (CS) is a support-free liquid–liquid chromatography based on the partitioning of solutes between two non-miscible liquid phases. The lack of any solid support provides many advantages over conventional LC such as high selectivity, high loading capacity, total recovery of the loaded sample and easy scale-up. CPC is used to perform rapid separation, isolation or enrichment of various bioactive compounds from very complex mixtures. Furthermore, the versatility of CPC technology allows to target different objectives in term of applications, whether by compounds differing in polarities and concentrations, by extract matrices, or by process. Few examples are presented to illustrate the flexibility and capacity of this technology.

Keywords: Centrifugal Partition Chromatography, Prep-chromatography, bioactive molecules, natural product, chromatography, fractionation

NON-TARGET IDENTIFICATION OF POLAR ORGANICS IN CIGARETTE LEACHATE BY HIGH-CAPACITY SORTIVE EXTRACTION AND TD-GC×GC–TOF MS

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Smoked cigarettes are the most common littered item found in urban environments and coasts worldwide. Today, there is conclusive evidence that when this type of waste comes into contact with water, a number of inorganic and organic compounds, are leached and become bioavailable to aquatic life [1]. The leachate from discarded cigarettes has been shown to be acutely toxic for diverse species such as marine bacteria (Vibrio fischeri), fish, snails and fish and frog embryos [2,3].

Cigarette leachates consist of highly complex mixtures of compounds across a wide concentration range, and such compounds typically elute as an unresolved complex mixture when subjected to one-dimensional gas chromatography (GC). As a result, cigarette leachate analysis poses a challenge for traditional sample extraction and chromatographic techniques.

In this study, comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC×GC-TOFMS) with high-capacity sorptive extraction was used for the exploratory profiling of leachate from used and unused cigarettes. The high-capacity sorptive extraction probes offer a larger volume of PDMS stationary phase (65 µL) compared to traditional SPME (~0.5 µL) enabling higher sample loadings. Used in conjunction with secondary refocusing, this approach offers excellent sensitivity for a wide range of chemical classes from volatiles to semi-volatiles, with improved chromatographic performance through trap-based focusing. GC×GC–TOF MS provides enhanced separation, improved peak capacity and the sensitive detection necessary to identify trace toxic compounds in these complex mixtures and to ultimately gain maximum insight into the composition of cigarette leachate.

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NEEDLETRAP – A UNIVERSAL TOOL FOR A WIDE RANGE OF APPLICATION FOR VOC-ANALYSIS

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After being introduced a few years ago NeedleTraps became more and more successful being used as a small, easy to handle and sensitive extraction tool.

During the past years a wide range of very different application, such as measurement of VOCs in seawater [1], natural water or wastewater [2], chemical defense in larvae secretions of the earwig [3], volatile fingerprints of different food matrices for certification of their origin and authenticity [4], analysis of Semi-volatile Organic Compounds in Air [5] or analysis of VOC extracted from the alveolar portion of human [6] or animal breath [7] were developed.

This presentation gives a compendium of various practices and sampling methods featuring the newly developed modular sampling case from PAS Technology Deutschland GmbH.

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COMPARISON OF VOLATILE ORGANIC COMPOUNDS EXTRACTION TECHNIQUES FOR THE COMPREHENSIVE CHARACTERISATION OF TOMATO PRODUCTS

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Extracting volatiles with green techniques is a fast-approaching way to assess aroma and flavour compounds in the food and beverage industry as part of product development, determination of shelf-life and product quality, investigation of off-odours and in the analysis of competitive products. Therefore, it becomes pivotal to determine which volatile extraction method is the most comprehensive in trapping the principal aroma features of a complex food product. A powerful combination of sample extraction, analytical fingerprinting and profiling approaches were used to determine the volatile profiles of tomato products. Comprehensive analysis and reliability were assessed and the multi-step enrichment SPME technique proved to be the most suitable for discrimination between similar tomato-based products, by providing the broadest chemical panorama. Multi-step enrichment will be shown to improve the discovery and confident identification of trace-level aroma and flavour compounds which are of vital importance in food quality evaluation.

MICROWAVE ASSISTED EXTRACTION A POWERFUL AND GREENER APPROACH FOR ENVIRONMENTAL SAMPLES, FOOD ANALYSIS AND ESSENTIAL OILS EXTRACTION.

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Microwave assisted extraction is a well-established extraction technique used in a wide range of applications. Over the past 20 years, hundreds of scientific articles have been produced to prove the effectiveness of this technique. Many of these demonstrate the ability of Microwave Assisted Extraction in maximizing the efficiency and reducing the extraction time over traditional techniques. Moreover, microwave ensures a greener approach to the extraction as it enables to dramatically reduces solvent volume and wastes, as well as offers a solvent free approach to extraction of natural products.

The challenge of the recent years has been to collect the modern labs requirements: high productivity, reliability and ease of use into a proper hardware. Thanks to the latest hardware developments, the potential of microwave extraction has further increased, making this technique a valuable asset for many labs, not only in comparison with traditional techniques but also over modern extraction technologies. Milestone's ETHOS X with the suitable accessories and extraction vessels allows the development of various methods within the same platform. Extraction of organic compounds from environmental samples, extraction of lipids and contaminants from food and feed samples, extraction of essential oils from cannabis and botanicals in general, are just some of the applications developed in recent years.

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DETERMINATION OF MICROPLASTICS IN WATER AND ENVIRONMENTAL MATRICES COMBINING THERMAL DEGRADATION WITH SOLID PHASE EXTRACTION AND GC/MS DETERMINATION OF POLYMER DEGRADATION PRODUCTS

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Targeted, sensitive and rapid determination of microplastics (MPs) in environmental samples, and in water, is achieved by indirect coupling of Thermogravimetric- and GC/MS analysis in the form of Thermal Extraction and -Desorption GC/MS (TED-GC/MS)[1,2]. Decomposition products of thermoplastic polymers and elastomers in samples up to 100 mg, in some cases more, are extracted, concentrated in a sorbent phase, and determined by Thermal Desorption (TD)-GC/MS. Limits of detection range from double digit ng to low single digit µg, corresponding to approximately 3-150 ppm in a 20 mg sample. Environmental samples such as air, water, and sludge or soil differ widely in terms of their MP content and sample homogeneity. TED-GC/MS method optimization for minimized matrix interference is discussed. Examples of MP mass content determination in water and environmental samples are presented. These include tire abrasion in sludge and road run-off[3] and thermoplastic polymers in various matrices across a wide range of concentrations, including, by fractionated filtration[4], across particle size ranges in water. Filter crucibles for direct analysis of water filtrates are presented[5]. Calibration examples based on reference standard material and a deuterated internal standard[6] are presented. Pyrolysis of polymers often results in complex GC/MS chromatograms and environmental matrices add to the complexity. This makes mass spectral identification via library comparison a challenge. A novel peak based data base approach is presented that provides targeted information for polymer identification in complex samples.

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MAGNETIC IONIC LIQUIDS FOR IMPROVING THE EXTRACTION PERFORMANCE OF ORGANIC POLLUTANTS IN LIQUID-PHASE MICROEXTRACTION

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Magnetic ionic liquids (MILs) have triggered enormous interest in Analytical Chemistry in the recent years due to their interesting features: (1) structure versatility, modulable viscosity, high solubility and ability for solvating compounds (properties resulting from their ionic liquid nature), and (2) effective magnetic susceptibility due to the presence of a paramagnetic component in either their cation or anion [1,2]. As a result of this last characteristic, MILs can be manipulated with a magnet and used in magnetic-assisted separation. Several analytical applications use MILs as extraction solvents during sample preparation [1,2]. In these cases, the success of the (micro)extraction protocol is related to the simplicity of the procedure, and the extraction performance. To improve both simplicity and extraction efficiency, parameters related to the method (e.g., dispersion type and magnetic separation method), and to the MIL design (e.g., MIL structure, viscosity and magnetic susceptibility) must be considered. In this talk, different MIL-based applications devoted to the extraction of organic pollutants are presented. The main important aspects related to the method development are discussed, and the results obtained with the analysis of real samples in combination with chromatographic techniques are also shown.

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MULTICLASS CYANOTOXIN ANALYSIS IN RESERVOIR WATERS: TANDEM SOLID-PHASE EXTRACTION FOLLOWED HYDROPHILIC INTERACCION LIQUID CHROMATOGRAPHY- MASS SPECTROMETRY

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The consumption of contaminated drinking water, skin contact and swallowing water during recreational activities are the most frequently reasons for human poisonings caused by cyanotoxins. According to the chemical structure, cyanotoxins are mainly divided into cyclic peptides, alkaloids, lipopeptides, non-protein amino acids and lipoglycans [1]. For risk assessment and studies on occurrence, the development of reliable, sensitive and cost-effective analytical approaches able to cover a wide range of cyanotoxins is essential. However, due to their different chemical structures and physicochemical properties, this task is being highly challenging [2]. In this sense, in the present work an UHPLC-MS/MS method has been developed for the simultaneous analysis of eight cyanotoxins belonging to different classes: microcystin-LR, microcystin-RR, nodularin, cylindrospermopsin, anatoxin-a and three non-protein amino acids such as β-methylamino-L-alanine and the isomers 2,4-diaminobutyric acid and N-(2-aminoethyl)glycine). An HILIC column is employed to allow the chromatographic separation in less than 15 min, using water and acetonitrile, both with 0.3% of formic acid, as mobile phase in gradient mode. Prior to the chromatographic separation, a novel sample treatment based on a tandem-SPE system has been investigated with the aim of extract and preconcentrate the chemically diverse group of cyanotoxins in freshwater reservoir samples. Nature of the cartridges and type and volume of elution solvent, among others factors, were examined to achieve the best extraction efficiency. In the optimized procedure two cartridges were connected in series: Strata-X cartridge (retaining non polar compounds) configured first in the line of sample flow, followed by the MCX cartridge (retaining non-protein amino acids). After conditioning step, sample was loaded onto the dual-cartridge set-up. For analytes elution the order of the cartridges changed, being MCX at the top and Strata-X at the bottom of the system. This step is mandatory to elute microcystin-RR and avoid its retention in MCX cartridge. Elution was performed using 10% $NH_3{\cdot}H_2O$ in MeOH.

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NOVEL EXTRACTION METHOD FROM WET HAEMATOCOCCUS PLUVIALIS USING GRAS SOLVENTS VIA MATRIX SOLID-PHASE DISPERSION

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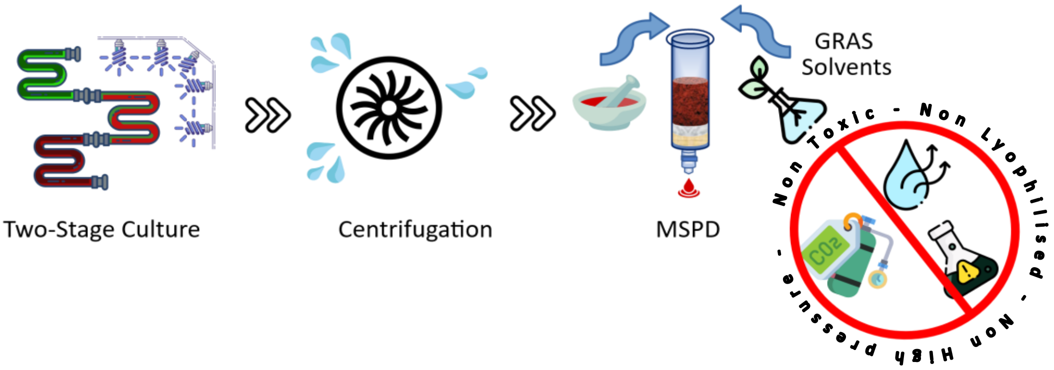
Haematococcus pluvialis is a microalgae source of carotenoids and fatty acids, characterised by a strong cell wall. The extraction of these compounds from this microalgae on an industrial scale requires tandem drying processes with energy-intensive extraction techniques. In contrast, this study uses a proven technique for the extraction of bioactive compounds from microalgae such as Matrix Solid-Phase Dispersion (MSPD).[1] MSPD is a scalable technique used in organic matrices with a moisture content above 60%, generating extracts that maintain the synergistic activity of the starting raw material.[2] Thus, from wet *H. pluvialis* in combination with *Generally Recognised as Safe* (GRAS) solvents, such as ethanol, ethyl lactate and ethyl acetate; an extract suitable for nutraceutical purposes can be obtained. By means of an optimisation process, the main extractive parameters (sample size, extractive volume, and dispersant/sample ratio) are modified to achieve a higher recovery of the main bioactive compounds of interest (fatty acids and carotenoids), as well as their antioxidant activity and total polyphenolic index. Through a comparative study with the main carotenoid and fatty acid extractive processes in *H. pluvialis*, including its lyophilised counterpart, the feasibility of the process is demonstrated.



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IN-VITRO HUMAN ORAL BIOACCESIBILITY OF PLASTICIZERS FROM MICROPLASTICS UNDER SIMULATED GASTRO-INTESTINAL DIGESTION.

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Human exposure to organic micropollutants through microplastics may occur via ingestion, inhalation, or dermal uptake. Among such micropollutants, plastic additives, and particularly plasticizers are of great concern due to the high amounts applied to plastics in order to increase their flexibility and softness and the proven endocrine-disrupting of many of these chemicals (González-Mariño 2019, Park 2020). In this work, standardized human *in-vitro* bioaccesibility tests under both fasting and fed conditions were applied for the investigation of the oral bioaccesibility of 8 phthalates and bisphenol A from low-density polyethylene (LDPE) and polyvinyl chloride (PVC) microplastic certified reference materials. Analysis of the bioaccessible phase was accomplished via dilute-and-shoot ultrahigh-performance liquid chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS) in the case of phthalates, and liquid-liquid extraction followed by derivatization and gas chromatography coupled to mass spectrometry (GC-MS) for bisphenol A. Non-bioaccessible fractions were determined in microplastics by ultrasonic solvent extraction and UHPLC-MS/MS and GC-MS. The results of our experiments showed that the oral bioaccesibility of phthalates and bisphenol A was higher in fed state and inversely proportional to $\log K_{ow}$ with maximum bioaccesibility values for dimethyl phthalate (DMP) and diethyl phthalate (DEP). Furthermore, bioaccesibility increased from gastric to gastrointestinal simulated digestion, being also higher for LDPE as compared to PVC. Finally, the determination of phthalate metabolites/degradation products showed that only DMP and DEP yielded a partial conversion (<10%) to the human metabolites (monoesters and phthalic acid).

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NATURAL DEEP EUTECTIC SOLVENTS FOR GREEN MICROWAVE-ASSISTED EXTRACTION OF ACTIVE COMPOUNDS FROM "HORCHATA DE CHUFA" BY-PRODUCTS

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In this work, a novel, efficient and environmentally friendly extraction process was optimized to obtain active compounds from food residues generated in "horchata de chufa" industry, a very popular drink consumed in the Mediterranean region and obtained from the tubers of *Cyperus esculentus L.* Microwave-assisted deep eutectic solvent extraction (DES-MAE) of polyphenols was applied for the first time on the above-mentioned residues. A screening test was initially performed where the use of various types of deep eutectic solvents (DES), prepared on choline chloride basis by adding different hydrogen bond donors (HBD), was evaluated using a Plackett-Burman design (PBD) in order to study the significant effect of different experimental variables. All DES were synthesized in the laboratory with a 1:2 molar ratio (ChCl:HBD) using inexpensive, environmentally friendly and natural components[1,2], and their proper synthesis was evaluated by FTIR and TGA characterization. The DES providing the best results for the extraction of the target compounds was selected for further testing. A Box-Behnken design (BBD) was then implemented to obtain optimal extraction conditions, such as extraction time and temperature, water content and liquid-solid ratio, which were optimized using response surface methodology (RSM). The extracts obtained under optimal conditions were evaluated on their antioxidant activity by using the DPPH method. Finally, the main polyphenols present in the these extracts were also identified and quantified by HPLC-MS. The proposed extraction approach of active compounds using DES-MAE could be a more sustainable and effective methodology compared to the use of other solvents such as ionic liquids or ethanol:water mixtures showing a great potential for the revalorization of "horchata de chufa" wastes.

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NON-TARGET SCREENING OF PHARMACEUTICALS IN SEWAGE SLUDGE: COMPARISON BETWEEN DDA AND DIA ANALYSIS

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Sludge is recognized as a sink of many moderate and highly lipophilic persistent compounds [1]. Due the fact that this residue contains a wide variety of organic and inorganic substances, and that the sludge from STPs is commonly re-used as agricultural fertilizer and raw material in compost, the study of these samples and the approach of new screening strategies is highly recommended. Target methods focused on the detection of specific compounds are totally blind to other species present in the sample [2,3]. However, screening strategies based on non-target analysis perform a complete search, recording in SCAN mode, mass spectral information along the entire chromatographic separation. This latter strategy constitutes a very appealing possibility for the detection of new pollutants.

Herein, the wide range of possibilities offered by QTOF-MS systems for non-target screening analysis are described for the particular case of sewage sludge. Matrix solid phase dispersion (MSPD) and ultra-performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry (UPLC-QTOF), were applied as sample preparation and determination techniques. In addition, different acquisition modes (data dependent, DDA, and data independent, DIA) will be described and compared. Finally, semi-quantitative concentration data will be presented for a selection of 37 compounds previously identified in samples from 16 STPs.

Acknowledgement:
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ASSESSMENT OF ION IMPRINTED POLYMERS TECHNOLOGY FOR THE DESIGN OF A NEW RADIUM SPECIFIC SOLID PHASE EXTRACTION SUPPORT

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During recent decades, human activities (e.g. mining, fracking) have contributed to the release of ^{226}Ra in the environment, one of the most radiotoxic natural radionuclides. Current issues regarding Ra are related to the understanding of its geochemical behavior and its transport mechanisms in the environment. This implies being able to precisely measure Ra at ultra-trace level in samples with complex matrices, whose available amount may be limited. Among the commercial resins, rare succeed alone to selectively extract Ra^{2+} from the other alkali or alkaline-earth cations and most extractions procedures are complex, multi-step and unsuitable for treatment of sub-mL sample volumes. Much attention has been drawn on grafting well-designed macrocyclic ligands on resins but this solution implies synthesizing complex molecules of significant cost and the grafting procedure can affect their binding properties. In this study, we investigated for the very first time the potential of ion imprinted polymers (IIPs) to selectively extract Ra^{2+}. Mass spectrometry and conductimetry techniques were first used to select the best monomers candidates, template/monomers ratios, and complexation time before performing bulk polymerization of the IIPs. As a comparative support, a non-imprinted polymer (NIP) was synthesized for each IIP under the same conditions, but without template ion. Performances of all supports were evaluated by solid phase extraction (SPE) and inductively coupled plasma mass spectrometry (ICP-MS). These characterizations highlighted a promising IIP enabling the separation of radium from alkalis and other metals (V, Mo, W, As, Sb, etc.). The repeatability of the synthesis was evaluated and a gain in specificity was obtained by varying the ligands proportion. After optimization of the SPE procedure and measurement of capacities and breakthrough volumes, the best IIP support was selected for an application to real samples and for comparison with commercial resins.

COMBINING PRESSURIZED LIQUID EXTRACTION AND ENZYMATIC-ASSISTED EXTRACTION TO OBTAIN BIOACTIVE NON-EXTRACTABLE POLYPHENOLS FROM SWEET CHERRY (*PRUNUS AVIUM* L.) POMACE

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Food processing results in large amounts of byproducts that could contain bioactive compounds. In this sense, sweet cherry pomace is a by-product that can be a source of bioactive phenolic compounds. Usually, polyphenols have been extracted using conventional extraction methodologies. However, a significant fraction of polyphenols, called non-extractable polyphenols (NEPs), remains retained in the conventional extraction residues.[1] To determine this underestimated fraction of phenolic compounds, the development of more sustainable, efficient, and selective extraction methodologies are needed.[2] Therefore, this work is aimed to investigate the extraction of NEPs from cherry pomace combining pressurized liquid extraction (PLE) and enzyme-assisted extraction (EAE) using Promod enzyme with protease and polygalacturonase activities.

A response surface methodology was employed to study the influence of three independent variables, temperature (60-80 °C), time (5-40 min), and (pH 6-10), on the NEPs extraction. The response variables were the total phenolic content (TPC) measured by the Folin-Ciocalteu method, total proanthocyanidin (PA) content evaluated by vanillin, DMAC, and butanol/HCl assays, and total antioxidant capacity determined by Trolox equivalent antioxidant capacity and inhibition of hydroxyl radical assays. The results indicated that the combination of PLE and EAE was more suitable and selective to obtain NEPs from sweet cherry pomace. In fact, the extracts obtained by the combination of these techniques displayed higher TPC, PA content, and bioactivity than the extracts obtained by PLE under the same extraction conditions. Moreover, size-exclusion chromatography profiles showed that the combination of PLE and EAE recovered NEPs with higher molecular weight than PLE without EAE treatment.

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SAMPLE TREATMENT STRATEGIES BASED ON LAB-ON-VALVE FOR DETERMINATION OF BIOACTIVE COMPOUNDS IN BIOMATRICES

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Sample treatment has been recognized as the most time-consuming and labour-intensive step in biological analysis [1]. New trends in sample preparation have focused on miniaturizing the analytical systems, which should favor automation, provide high-throughput performance, and enable online coupling with analytical instruments. Lab-on-valve (LOV) is a mesofluidic platform that allows the miniaturization and integration of analytical processes through automation [2]. LOV is a suitable approach for implementing automatic micro-solid phase extraction (µSPE) methodologies using the bead injection (BI) concept [3] with renewable sorptive phases. Due to the mesofluidic scale of LOV channels that are suitable for the fluidic manipulation of solid phases, BI-SPE procedures in LOV present enhanced precision with exact control of time events [2]. In the present work, automatic methods of sample treatment using LOV platform targeting the determination of different bioactive compounds in biomatrices will be discussed. First, an automatic µSPE-BI-LOV method using hydrophilic-lipophilic balanced mixed-mode sorbent decorated with sulfonic acid groups (Oasis MCX) was developed for the determination of tranexamic acid in urine. All µSPE-BI-LOV steps were implemented by computer programming, rendering enhanced precision on time and flow events. The application to human urine samples collected during scoliosis surgery has been pursued. Also, a methodology for determination of uremic toxins in plasma is currently under development.

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PAPER-BASED MICROFLUIDIC DEVICES AS EFFECTIVE EXTRACTION METHOD FOR NUCLECAID BASED PATHONGE DETECITON FOR WATER QUALITY

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Contamination of pathogens in water resources and related diseases is a major global water quality issue. Diseases caused by various bacteria, viruses, protozoa and helminths in rivers, lakes, groundwater and seawater have resulted in many disease outbreaks. Conventional methods for pathogen detection are often laborious and expensive, which prevents their widespread use in the field. Recently, the directional flow of fluid in microfluidic paper-based analytical devices (µPADs) contributes to their ability to perform nucleic acid extraction. In addition, sample pretreatment nucleic acid extraction, amplification and analysis can be integrated on µPADs. Therefore, we applied the loop-mediated isothermal amplification (LAMP) assay on a µPAD for multiplex determination of three bovine infectious reproductive diseases in bull semen [1]. Later, we developed a µPAD for on-site identification of Plasmodium falciparum and Plasmodium pan from whole blood in Uganda [2]. Recently, we have developed a µPAD that combines DNA extraction, LAMP amplification and fluorescence analysis, which enables a sample-to-answer assay within 1 hour for bacteria detection. This device can be used for multiplex detection of Salmonella, Escherichia coli (E. coli) and Clostridium perfringens (C. perfringens) with detection limits of 100 copies DNA μL^{-1}. Moreover, this device is currently under development to track the source of Severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) based on wastewater-based epidemiology [3,4]. Therefore, µPADs can be used as an effective nucleic acid extraction method, which can be further integrated into field application modules for sample preparation and rapid detection of pathogens in water.

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ELECTROMEMBRANE EXTRACTION OF POLAR SUBSTANCES – CURRENT STATUS AND FUTURE PERSPECTIVES

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Efficient and selective extraction of polar substances from complex samples is generally recognized as more challenging to accomplish than for corresponding hydrophobic substances. Sample preparation for this class of analytes is therefore typically simple pretreatment, such as protein precipitation or dilute-and-shoot. New and better methods based on extraction are however in development. Electromembrane extraction (EME) is one example. EME is based on electromigration of charged analyte species across a supported liquid membrane (SLM), into a clean acceptor solution. In the past 15 years, the technique has been well merited for selective extraction of hydrophobic substances. In recent years, increasing focus has however been diverted to its application for extraction of polar substances, which has required the development of new systems. This presentation will feature a discussion on different strategies for EME of polar substances, current capabilities and limitations, and future perspectives on this application. This will include selection/design of solvents, and clean-up capabilities from complex matrices.

ELECTROMEMBRANE EXTRACTION OF PHARMACEUTICALS AND ENDOGENOUS METABOLITES WITH CHITOSAN TAILOR-MADE MEMBRANES AS BIOPOLYMERIC SUPPORT

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Chitosan is a polysaccharide derived from chitin, which can be obtained both from natural sources (such as crabs, shrimps, lobsters or fungi), and after a deacetylation process of chitin with a variable degree of deacetylation (70-95%), on which many of its physical and chemical properties, as well as its reactivity, will depend [1]. Due to the presence of hydroxyl and amino groups (-OH and -NH_2) in the polymeric chain, hydrogen bonds can be easily formed. Moreover, it is also capable of gelling [2], so it could be interesting as an alternative for application in electromembrane extraction (EME) systems. In this work, a new chitosan-based membrane composed by 60% (w/w) of chitosan and 40% (w/w) of Aliquat®336 is proposed for the first time as new biopolymeric support for EME. The synthesis of the membrane was optimized in terms of composition and thickness, being characterized by Scanning Electron Microscopy (SEM). This new support was used in the simultaneous extraction of different pharmacological compounds such as non-steroidal anti-inflammatory drugs (salicylic acid (SAL), ketoprofen (KTP), naproxen (NAX) and ibuprofen (IBU)) as well as polar acidic drugs (nicotinic acid (NIC), amoxicillin (AMX), hippuric acid (HIP) and anthranilic acid (ANT)). Extraction parameters as organic solvent, pH of donor and acceptor solutions, voltage and extraction time were investigated in order to set the optimal conditions. Once optimization was carried out, the target analytes were successfully extracted performing the EME procedure at 100 V for 10 minutes with chitosan membranes of 30-35 µm as support of 1-octanol liquid membrane. High enrichment factors were obtained for most of the compounds, with ranges between 118 and 113 for HIP, NIC and SAL, and ranges between 49-20 for ANT, AMX, KTP, NAX and IBU. Moreover, the target analytes were satisfactorily extracted from human urine samples, providing high extraction efficiency.

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A NEW VALIDATED WIPE SAMPLING PROCEDURE COUPLED TO LC-MS/MS FOR ASSESSING SURFACE CONTAMINATION BY 13 CYTOSTATICS

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Cytostatics are drugs used in cancer treatment, which pose serious risks to healthcare workers due to their carcinogenicity, mutagenicity and genotoxicity. Dermal absorption via surface contamination is the key route of exposure and widespread prevalence of cytostatics indoors has been reported worldwide [1]. Hence, monitoring is crucial to identify the occupational exposure risk and implement preventive measures. As such, rapid, reliable, and validated analytical methods for multicomponent detection are needed. A surface wipe sampling technique (commercial gauze wetted with 1 mL isopropanol), compatible with hospitals' safety requirements, coupled to liquid chromatography-tandem mass spectrometry analysis was developed, allowing the identification and quantification of 13 cytostatics in workplace surfaces. The extraction method was fast, simple, and needed little solvent volume: 1 mL acetonitrile, 20 min ultrasonic bath, evaporation and reconstitution in 200 µL acetonitrile. Good linearity, sensitivity and precision were achieved for all compounds, with detection limits from 0.1 to 4.0 pg/cm^2. Accuracy, assessed by the percentage of recovery (calculated by the method of standard addition), for four model surfaces (melamine-coated wood, phenolic compact, steel 304, steel 316), was generally acceptable (average %R 80±12%, except for two analytes). Global uncertainty is below 35% for concentrations above 100 pg/cm^2 (except for two cytostatics), which is a guidance value for relevant contamination. Method application in a hospital indicated 3 (out of 28) samples at concentrations higher than the guidance value and seven cytostatics were identified.

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ANALYSIS OF MICROBIAL CONTAMINATED COSMETIC CREAMS BY ION MOBILITY SPECTROMETRY AND MASS SPECTROMETRY COUPLED TO GAS CHROMATOGRAPHY

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Cosmetic products can be contaminated with filamentous fungi, yeasts and bacteria from many different sources, including the natural raw materials, equipment, water, operators or even air. Nowadays, the most commonly used technique for monitoring microbial contamination in cosmetic products is plate counting. In this contribution, headspace - gas chromatography (HS-GC) coupled to mass spectrometry (MS) or ion mobility spectrometry (IMS) is proposed as a technique to evaluate rapid and accurately the state of microbial colonies in cosmetic creams using the volatile organic compounds produced by microorganisms (MVOC). The work focuses on monitoring two of the microorganisms that most frequently occur in cosmetic creams, *Candida albicans* and *Staphylococcus aureus* [1]. In addition, two different types of ingredient with antimicrobial properties (a chemical preservative and a natural preservative) were added to study the behavior of these microorganisms under different conditions. The facial creams were elaborated and inoculated with the two above microorganisms, and then sampled weekly for 4 weeks, analyzing the evolution of the MVOCs by HS-GC-MS and HS-GC-IMS. Moreover, microbial contamination was determined by the classical plate counting method. The pH, color, viscosity and water activity parameters were also measured. The use of chemometric tools is fundamental because of the large amount of data generated, and different models based on discriminant analysis with an orthogonal projection on latent structures (OPLS-DA) were constructed. The optimal models obtained by both analytical techniques allowed differentiation between contaminated and non-contaminated creams, with a validation success rate of 94.4%. Furthermore, MVOC monitoring also allowed assessment of the microbial concentration.

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FROM PLANTS SAMPLES TO ANALYSIS OF BIOLOGICALLY ACTIVE COMPOUNDS – TOWARD GREEN(ER) ANALYTICAL CHEMISTRY

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It is well-known that plants are promising source of biologically active compounds. How to take them from natural sources? There are many available techniques with their advantages and disadvantages. We need multidisciplinary approach, combining our knowledge about specific plant and chemistry which can be applied in sample pretreatment, extraction of valuable compounds and measurements of targeted analytes. If we want to make it greener, we're facing with more challenges to fit high analytical demands, especially in terms of specificity selectivity and accuracy. In this work, two case studies will be presented. The first one will be oriented toward application of subcritical water extraction (SCW) of flavonoides from Chamomile Ligulate Flowers and utilization of UHPLC-HESI-MS/MS for analysis of chemical profile of chamomile SCW extract and HPTLC-UV/VIS in quantitative analysis of apigenin, as one the most potent flavonoid [1]. In the second case, challenges in analysis of biogenic volatile compounds (neral, geranial, α-pinen and 1,8 cineole) by Headspace GC-MS analysis will discussed, in line between the theory of static headspace extraction and analytical application [2].

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DEVELOPMENT OF HYBRID MONOLITHS INCORPORATING METAL-ORGANIC FRAMEWORKS FOR STIR BAR SORPTIVE EXTRACTION COUPLED WITH HPLC FOR DETERMINATION OF ESTROGEN ENDOCRINE DISRUPTORS IN ENVIRONMENTAL AND BIOLOGICAL SAMPLES

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The endocrine-disrupting effects caused by synthetic chemicals on the endocrine systems of human and wildlife have received great attention worldwide [1]. Particularly, estrogens have shown an intense endocrine-disrupting potency, interfering with the normal functions of the biological systems. These compounds are released from wastes of human and livestock, pharmaceuticals, and agricultural chemicals. Therefore, their evaluation in the environment is of great significance for the health of humans and ecological protection. The monitoring of estrogen residues in environmental matrices requires the development of a pre-treatment step to enhance sensitivity and reduce interferences. Many pretreatment methods have been used for extracting trace estrogens in environmental samples, such as solid-phase extraction, dispersive liquid–liquid microextraction, solid-phase microextraction and stir-bar sorptive extraction (SBSE) [2]. However, the commercially available coatings in SBSE have low selectivity, slow extraction kinetics and low extraction efficiency for these targets.

In this study, a novel coating based on hybrid monolith with metal-organic framework (MOF) onto conventional Teflon coated magnetic stir bars was developed. For this purpose, the external surface of the Teflon stir bar was firstly vinylized in order to immobilize a glycidyl methacrylate(GMA)-based polymer onto the magnet. Then, an amino-modified MOF of type NH_2-MIL-101(Al) was covalent attached to the GMA-based monolith. The experimental conditions of the functionalization reaction of parent monolith with this MOF were also optimized. The resulting hybrid monolith was evaluated as SBSE sorbent to extract four estrogens (such as natural 17-β-estradiol, metabolites as estrone and estriol, and synthetic 17α-ethinylestradiol). Next, several parameters affecting extraction of target estrogens by SBSE including extraction time, pH, stirring rate, pH, ionic strength, desorption solvent and desorption time were investigated. Under the optimal experimental conditions, the analytical figures of the method were established, achieving satisfactory limits of detection (in the range of 1–10 μg L^{-1}) and enrichment factors (*ca*. 100) were established. The proposed method was successfully applied to the analysis of estrogens in environmental (water) and biological (urine) matrices, and quantitative recoveries were obtained from spiking experiments.

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IN-SYRINGE AUTOMATION OF SAMPLE PREPARATION FOR ENVIRONMENTAL ANALYSIS

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The Lab-In-Syringe technique is the latest development in flow automation approaches [1,2]. This flow-batch approach is based on carrying out mixing, reaction, or/and extraction steps in the void of an automated syringe pump acting as size-adaptable yet steadily sealed chamber. This allows straightforward automation of classical laboratory tasks including the sample preparation procedures directed to analyte preconcentration and matrix elimination.

Placing a magnetic stirring bar inside the syringe and software-aided rotation control enables instantaneous, homogenous, and on-demand in-syringe mixing of step-by-step added reagents including immiscible solvents and sorbent. Moreover, it does not dependent on solution viscosities nor volume ratios [2]. Consequently, the Lab-In-Syringe technique has been used advantageously for the automation of practically all standard procedures including dispersive liquid-liquid microextraction, single-drop microextractions, dispersive solid phase extraction, cloud point extraction, or head-space separations, which are surveyed in a recent tutorial [3].

We give an overview on preparation methodologies and operation modes performed by the Lab-In-Syringe technique coupled online to liquid and gas chromatography as well as spectrophotometric determination of environmental contaminants BTEX, nitrophenols, and pharmaceuticals, among others. A critical comparison to sample preparation procedures based on versatile autosampler systems will be given regarding operational limitations and complementary potentials.

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RECENT ACHIEVEMENTS IN VERSATILITY THROUGH STIR BAR SORPTIVE DISPERSIVE MICROEXTRACTION APPROACH

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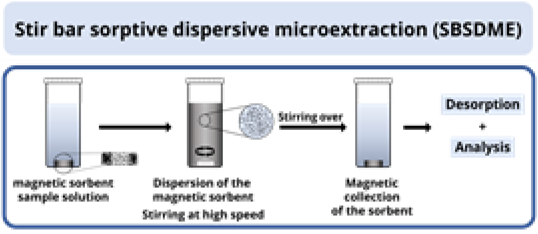
Stir bar sorptive dispersive microextraction (SBSDME) was presented by our group few years ago as a hybrid sorbent-based microextraction procedure that imbues both stir bar sorptive extraction and dispersive solid phase extraction with distinct advantages such as lower extraction time, more versatile sorbents by using magnetic materials, and easier extraction and post-extraction treatment [1]. Over the last six years, the great diversity of analytes and matrices in which the technique has been successfully applied demonstrates its great versatility [2]. In this context, different tailor-made magnetic sorbents have been used in SBSDME to achieve the selective and quantitative extraction of different analytes, in such a way that SBSDME-based methods stand out for their very satisfactory analytical features. This contribution presents the very recent achievements of our group in terms of versatility of this approach to the trace determination of compounds in different fields of application (e.g., polycyclic aromatic hydrocarbons in cosmetics, tetrahydrocannabinol in cannabidiol-based cosmetics, tricyclic antidepressants in urine, etc.), by using different magnetic sorbent materials (e.g., polymer-based sorbents, carbonaceous materials, etc.).



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ON-LINE SFE-ENANTIOSELECTIVE-SFC-QQQ MS FOR THE DETERMINATION OF CHIRAL PESTICIDES IN HEMP SEEDS: A PROOF-OF-PRINCIPLE STUDY

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Hemp seeds are considered as a novel food, and as for all derivatives of vegetable cultivations, could potentially contain pesticides. Various pesticides possess one or more chiral centers in their structure. In such a respect, pesticide enantiomers can be characterized by a different activity, exhibiting a diverse toxicity. The present research can be considered as a proof-of-principle study focused on the determination of chiral pesticides using a supercritical fluid extraction instrument coupled on-line with an enantioselective supercritical fluid chromatography-triple quadrupole mass spectrometry one. To the best of the present Authors' knowledge, this is the first description of an on-line approach for the simultaneous extraction and determination of chiral pesticides. Metalaxyl, benalaxyl and dimethenamid chiral contaminants were searched for in nine hemp seed samples belonging to three varieties of Cannabis sativa; only in one case a pesticide was found at levels above the method limit of quantification (LoQ), though within the European Union maximum residue level value. The figures-of-merit determined were linearity, precision, limit of detection (LoD), and LoQ. Specifically, regression coefficients were between 0.9856 and 0.9973, the LoDs were in the 0.04-0.41 μg kg^{-1} range, the LoQs were in the 0.12-1.38 μg kg^{-1} range, while coefficients of variation were between 1 and 3% (at the 10 μg kg^{-1} level).

QUANTITATION OF TRANSFORMATION PRODUCTS OF UNSYMMETRICAL DIMETHYLHYDRAZINE IN SAND USING VACUUM-ASSISTED HEADSPACE SOLID-PHASE MICROEXTRACTION

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Quantification of unsymmetrical dimethylhydrazine (UDMH) transformation products (TPs) in solid samples is an important stage in monitoring environmental pollution by heavy rockets launches. Most prospective sample preparation methods for determination of UDMH TPs in soil samples are based on headspace solid-phase microextraction (HSSPME) [1]. Conducting HSSPME under vacuum (Vac-HSSPME) provides lower detection limits of polar analytes with low Henry's law constants [2]. Previously developed method based on Vac-HSSPME [3] has the decreased accuracy of analysis due to the side processes occurring after addition of water to the soil. This study was aimed at developing the method based on Vac-HSSPME that does not require an addition of water.

Compared to the regular HSSPME, Vac-HSSPME yielded 1.3-4.8 times higher responses for NDMA, MTA and PAl. Increasing air-evacuation time from 20 to 120 s at 23 °C resulted in decreased responses of analytes by 25-46%. The best combination of responses of analytes and their RSDs was achieved after air-evacuation of a sample (m = 1.00 g) for 20 s at 23 °C, incubation for 30 min and 30-min extraction at 40 °C by Car/PDMS fiber. Vac-HSSPME provided linear calibration plots in studied ranges of concentrations with R^2 ranging from 0.9912 to 0.9938. The LODs for spiked sand samples varied from 0.035 to 3.6 ng g^{-1}. Spike recoveries of target analytes from sand samples were 84-97% with RSDs 1-11%. The developed method was successfully applied for studying losses of analytes from open vials with model sand spiked with UDMH TPs. The developed method can be recommended for analysis of trace concentrations of UDMH TPs when studying their transformation, migration and distribution in a contaminated sand.

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IN-SITU EXTRACTION APPROACHES FOR ENVIROMENTAL WATERS ANALYSIS

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Environmental monitoring is crucial to assess the quality of natural waters, considered by the European Union as a heritage to be protected [1]. The size of the aquatic environmental compartments challenges the representativeness of the sample acquisition, making multisampling a necessary strategy. In situ extraction techniques allows isolating the target analytes at the sampling point, simplifying the logistics (the extraction media and not the sample is transported to the laboratory for final analysis) and ensuring the chemical integrity of the sample (avoiding losses of the analytes by adsorption or evaporation). In the last years, our research group has developed different alternatives in this context based on the use of solid traps (nano and microparticles and membranes) for the efficient isolation and concentration of target compounds. This communication will present a general overview of these approaches making emphasis on the last developments where new materials are used as sorptive media. The application of commercial membranes, magnetic paper-based sorptive phases (Figure) and microparticles supported films will be discussed and compared.

Figure. Magnetic paper-based sorptive phases based on the coating of a paper substrate by a magnetic nanocomposite.

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MULTI-CUMULATIVE TRAPPING HS-SPME: A NOVEL APPROACH TO ENHANCE VOLATILE FINGERPRINTING

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Multiple-cumulative trapping headspace-solid-phase microextraction (named MC-SPME) is a very powerful technique to enhance the level of information on the volatile profile. A fully automated multi-mode sample preparation system, containing a sorbent based focussing trap to retain and preconcentrate analytes, was used. Different extraction parameters were investigated, i.e., extraction time, numbers of cumulative extraction, and the sample volume. Shorter cumulative extraction times proved to be more effective than a single longer extraction to provide more comprehensive profile of volatiles, particularly by increasing the uptake of the semi-volatiles. Optimization of the sample volume was necessary to avoid headspace saturation and thus maximize the extraction of the semi-volatile compounds. This technique was successfully applied for the distinction of extra virgin olive oil, from the less expensive virgin olive oil and lampante oil [1,2]. Finally, the coupling of MC-SPME with GC×GC-MS provided a powerful platform for the detailed characterization of food aroma profile.

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CHEMICAL MODIFICATION OF 3D PRINTED STRUCTURES WITH SMART MATERIALS FOR SAMPLE PREPARATION

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3D-printing is an incipient technology in analytical chemistry for the fabrication of novel 3D printed structures, which cannot be easily created by other technologies or can be fabricated at low-cost. There are different 3D printing technologies available such as fused deposition modelling, vat polymerization, photopolymer inkjet printing and selective laser sintering, all with their own merits and drawbacks. In the last years, the use of 3D printing in sample preparation has increased significantly so that 3D printed objects have been proven superb as extraction materials [1, 2], although the raw prints afford poor extraction recoveries due to their low surface-area. To tackle this drawback, many authors have chemically modified the surfaces of the 3D printed templates or devices with smart materials such as porous monoliths, nanomaterials, metal organic frameworks or even selective materials such as molecular imprinting polymers, aptamers and antibodies. The main problem is the diversity of the materials used in the 3D printing process, which depends strongly on the printing technology. For this reason, different approaches to modify the prints have been explored in the literature in order to obtain an adequate coverage with smart materials, as will be comprehensively illustrated in this lecture with a number of examples from distinct research fields.

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SYNERGISTIC COMBINATION OF POLYAMIDE-COATED PAPER-BASED SORPTIVE PHASE FOR THE EXTRACTION OF ANTIBIOTICS IN SALIVA

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This contribution describes the design and proof-of-concept of the synergistic extraction of a planar paper-based sorptive phase modified with a polyamide such as nylon [1]. The as-prepared material permits the joint isolation of six penicillin-derived antibiotics of different polarity from human saliva in a single extraction. The different analytes either interact with the cellulose substrate or the polyamide coating depending on their chemical structure. The sorptive phase is prepared by dip-coating, a well-established and affordable technique that can be applied in any laboratory using cheap reagents and precursors [2]. The use of the material as the sorptive phase combined with liquid chromatography-tandem mass spectrometry enables the determination of the analytes in saliva samples with limits of detection from 2.4 to 3.7 ng mL^{-1}. Relative standard deviations (RSD) below 10 % for all the target analytes and relative recoveries between 84 and 123 % were achieved by using matrix-matched calibration. These results confirm the versatility of the polyamide-coated paper-based sorptive phase, and its potential to be applied in bioanalysis. Moreover, the easy preparation of the sorptive phase and their low cost, as well as the high sample throughput analysis, are some of the main features of the proposed method.

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PREPARATION AND EVALUATION OF MIXED-MODE MATERIALS TO SELECTIVELY EXTRACT ACIDIC COMPOUNDS BY STIR BAR SORPTIVE EXTRACTION FROM ENVIRONMENTAL WATERS

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Mixed-mode ion exchange materials were introduced to improve the selective extraction of ionic compounds. They integrate ionic moieties into a polymeric or silica backbone combining ionic with reversed-phase interactions. However, so far, only few mixed-mode materials are applied to stir bar sorptive extraction or related technologies [1,2]. In this study, two novel mixed-mode weak anion-exchange materials, EDA1 and EDA2, have been prepared and evaluated by stir bar sorptive extraction (SBSE) followed by liquid chromatography-mass spectrometry in tandem for the extraction of a group of acidic compounds. Both materials present secondary amines as ionizable functional groups anchored in a polymeric monolith. The SBSE parameters were carefully optimized to exploit the ionic interactions between the acidic compounds and the functional groups of the materials, and attain the selective extraction of the target analytes. Special attention was paid to the pK_a values of both the analytes and the functional groups of the materials. The following extraction optimum conditions: 10 mL of ultrapure water adjusted to pH 6 stirred at 600 rpm for 180 min; desorption with 3 mL ACN containing 5% NH_4OH in the ultrasonic bath for 20 min, were used to determine acidic compounds in environmental water samples using the stir bar which provides better results.

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THIN-FILM MICROEXTRACTION USING MOF-BASED POLYMERIC COMPOSITES AND LIQUID CHROMATOGRAPHY FOR THE DETERMINATION OF PERSONAL CARE PRODUCTS IN COSMETICS

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Thin film microextraction (TFME) is an analytical sample preparation technique that allows trapping target compounds from aqueous samples with high preconcentration, by using a high exposure surface of sorbent materials (still in the microextraction range) while ensuring shorter extraction times, particularly when compared with other conventional solid-phase microextraction approaches. However, the selectivity and permeability of the most widely neat polymeric films used in TFME are low. In order to improve their performance, different kinds of extractant materials have been incorporated in these polymers, forming mixed-matrix membranes (MMMs) composites. Among them, metal-organic frameworks (MOFs) have gained a privileged position as additives in MMMs [1]. MOFs are formed by metal ions (or metal clusters) and organic linkers connected by coordination bonds, generating a three-dimensional crystalline network full of pores. MOFs have an incredible tuneability while presenting the highest surface area known. In this study, MOF-based MMMs are used as sorbent materials in a TFME device for the determination of personal care products in cosmetics, combining the technique with high-performance liquid chromatography and UV-Vis detection.

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PROFILING OF CARNITINE AND ACYLCARNITINES IN GLIOMAS USING SOLID PHASE MICROEXTRACTION (SPME) –THE PILOT STUDY

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It was reported that carnitine and acylcarnitnes levels are elevated in cancerous tissues in comparison to healthy ones. Therefore, in this work carnitine and its esters profiling was carried out in brain tumors (gliomas) with regards to their grade, presence of IDH mutation and 1p / 19q co-deletion. As a sampling method, chemical biopsy was used to assess its utility in this application. For this purpose brain tumors obtained from 19 patients were sampled on-site with SPME fibers directly after removal of the tumors. Next, probes were desorbed and analyzed with the use of liquid chromatography coupled with Q Exactive Focus. Full scan analysis followed by the MS/MS confirmation of tentative acylcarnitines was performed. Identification was based on fragmentation patterns match with spectra libraries with <3 ppm mass accuracy. Chemical biopsy enabled identification of carnitine and its 22 esters. It was found that short and long acyl chains acylcarnitines created two separate clusters which might be related to the dependence on carnitine-shuttle system enzymes activity. It was also observed that tumors with higher grade as well as those with worse clinical prognosis (lack of IDH mutation and without 1p/19q co-deletion presence) were characterized by higher level of studied analytes. In conclusion, the profile of carnitine and its derivatives varies in gliomas in regard to grade and genetic changes. Moreover, chemical biopsy as a no-tissue consuming and low invasive method could be useful tool in carnitine and acylcarnitines profiling.

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NEW TRENDS IN FOOD ANALYSIS BASED ON MICROEXTRACTIONS THECNIQUES

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The study and classification of food products quality and origins is carried by food chemistry. Determination of food contaminants has a main role in food safety since they represent a risk to consumers' health. Food analysis requires constant improvement in determination methods in terms of effectivity, rapidity, ruggedness, and reliability. At the same time, it must follow Green Analytical Chemistry Trends related to waste, organic solvents volumes, and stages of analysis reduction, among others.

Food products have a very complex composition, so a large sample preparation process is often needed. In this context, microextraction techniques represent an attractive alternative by significantly reducing sample and organic solvents volumes, as well as time and analysis conditions.

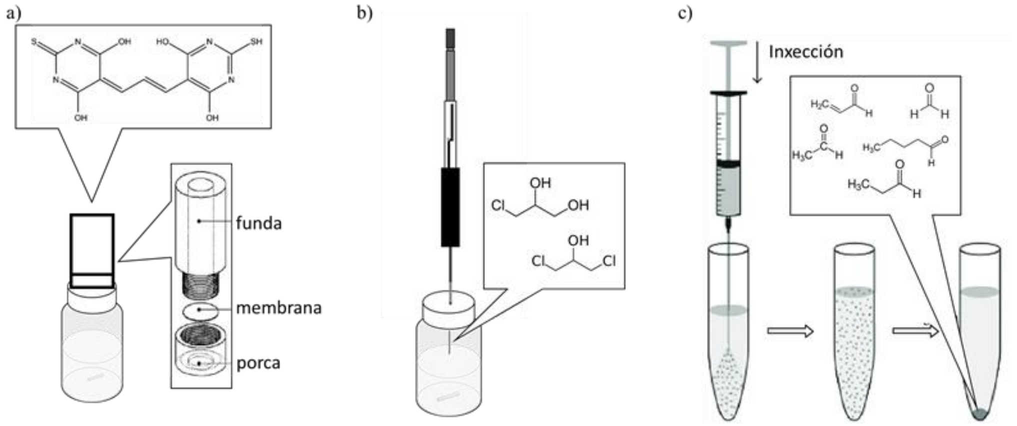

Figure 1. Scheme of extraction of food contaminants using GDME (a), MSPD (b) e DLLME (c).

Here, dispersive liquid-liquid microextraction (DLLME), gas-diffusion microextraction (GDME) and solid-phase microextraction (SPME) are presented as a novel proposal in food analysis.

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APPLICATION OF VACUUM-ASSISTED HEADSPACE SOLID PHASE MICROEXTRACTION TO CHARACTERISE THE VOLATILE AND SEMI-VOLATILE FRACTIONS OF COMPLEX SOLID PLANT MATRICES

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The characterisation of the semi-volatile fractions of plant raw materials and derivatives is, in some cases, fundamental in defining their origin, trade value and potential applications. This is true for Frankincense resins whose semi-volatile fraction compositions discriminate samples of different origins and market prices [1]. Similarly, the semi-volatile content of *Cannabis sativa* L. plant materials determines whether the plant is intended for fibre/seed production, therapeutic purposes or recreational use [2]. Head space solid-phase microextraction (HS-SPME) is extensively used in combination with gas chromatography-mass spectrometry (GC-MS) to analyze volatiles and semivolatiles. However, its relatively low sensitivity with less volatile compounds often requires long sampling times and high temperatures for their extraction. HS-SPME carried out under reduced pressure, also known as vacuum-assisted HS-SPME (Vac-HS-SPME), has been shown to accelerate the extraction rate of those compounds with low volatility (i.e. semi-volatiles) providing higher extraction efficiency and improved sensitivities in shorter sampling times and at reduced temperatures compared to regular HS-SPME [3]. As for regular HS-SPME, Vac-HS-SPME can be online-combined to gas chromatography-mass spectrometry (GC-MS) instrumentation and the only additional step required is air-evacuation of the vial before or after sample introduction [3]. This work explores the application of Vac-HS-SPME combined with GC-MS to characterize the volatile and semi-volatile pattern of solid matrices of plant origin including Frankincense resins and *Cannabis sativa* samples. The results prove that Vac-HS-SPME can succesfully be applied to complex plant derived solid matrices and show that with a suitable optimisation of the sampling parameters (i.e. sample temperature during the air-evacuation step and sample amount) sampling under vacuum condition enhances the extraction efficiency of semi-volatiles in shorter sampling times without significant losses of the most volatile components during the air-evacuation step.

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MINIATURIZED AQUEOUS BIPHASIC SYSTEM CONSISTING OF FOOD ADDITIVES FOR THE PRECONCENTRATION OF PERSONAL CARE PRODUCTS IN WASTEWATERS

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Aqueous biphasic systems (ABSs) are ternary systems composed of water and two water-miscible solutes that can separate in two coexisting phases. ABSs have been widely used as extraction platforms since depending on the composition of the ABSs, the target compounds present specific partition behaviors and can be concentrated in one of the solute-rich phases, leading to quantitative extraction. Despite these features, their preconcentration capabilities to develop microextraction strategies (μ-ABS) have been scarcely exploited. Polymers, ionic liquids, and deep eutectic solvents are the most common solutes used to prepare ABSs intended for extraction. However, they present certain limitations, such as high viscosity, low water stability, and controversial toxicity [1]. In this study, a green, simple, and low cost microextraction and preconcentration strategy based on a μ-ABS is developed for the extraction and preconcentration of pollutants of emerging concern in wastewater samples. The entire procedure is free of organic solvents and only requires mixing two food additives in the water sample: cholinium chloride (1.55%, w/w) as the extraction phase and K_2HPO_4 (59.5%, w/w) as the salting-out agent. These reagents are characterized for their low toxicity and low cost as they are produced at a large scale. The μ-ABS is combined with high-performance liquid chromatography and diode array detection for the determination of parabens, UV-filters, and one disinfectant. Apart from its sustainability, the method is also highly efficient, leading to enrichment factors up to 100 and quantitative extraction for those compounds containing OH groups in their structure, which can undergo hydrogen bonding to cholinium chloride.

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NATURAL DEEP EUTECTIC SOLVENT (NADES) AS A NOVEL DISPERSER IN LIQUID–LIQUID MICROEXTRACTION BASED ON SOLIDIFICATION OF FLOATING ORGANIC DROPLET (DLLME-SFO)

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New trends in analytical chemistry encourage the use of green solvents instead of toxic organic solvents to developed new methods aligned with Green Chemistry. In this sense, Natural Deep Eutectic Solvents (NADESs) have emerged as a new generation of green solvents composed by natural compounds such as sugars, alcohols, amino acids, organic acids, and choline derivatives, which offer numerous advantages including biodegradability, low toxicity, solute stabilization, sustainability, low costs and simple preparation. With the aim of evaluating the potential applicability of NADESs in sample treatment, a DLLME-SFO method using a NADES as dispersive solvent has been proposed for the extraction of the insecticide fipronil and its metabolites fipronil-sulfone and fipronil-sulfide, together with the fungicide boscalid from environmental water and white wine samples prior to their analysis by HPLC-UV. These target compounds have special interest in food and environmental safety since they are related to the Colony Collapse Disorder (CCD) in bees. The variables involved in the extraction and chromatographic separation were carefully optimized. Thus, the dispersion capacity of several NADESs was evaluated and 2 mL of the so-called "LGH" solution, composed by lactose, glycerol and water at a molar ratio of 5:1:3 were selected as dispersive solvent while 100 µL of 1-dodecanol were used as extraction solvent. Both solvents were mixed and rapidly injected into 5 mL of a sample solution saturated with 0.75 g of Na_2SO_4 causing a cloudy solution. The ternary sistem was vigorously shaken, centrifuged and placed into an ice bath allowing solidification of the droplet of 1-dodecanol, which was redisoluted in MeOH before its injection into the HPLC-UV system. The chromatographic separation was carried out in a C18 column with a mobile phase consisting of MeOH/H_2O (65:35, v/v) in isocratic mode. LOQs lower than 4.5 µg/L and recoveries above 80% with a RSD below 15% were achieved in both samples showing that the proposed method is a powerful, easy and green alternative for the determination of these compounds, demonstrating the new application for NADESs in sample preparation.

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THE INFLUENCE OF DISINTEGRATION METHOD TO THE EXTRACTION EFFICIENCY IN METABOLOMICS ANALYSIS

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Scientists are looking for a tool that will allow them to effectively, quickly, accurately and low-cost determine the type of bacteria. Finding such a method of identifying microorganisms will significantly accelerate the implementation of treatment and allow for better effectiveness. One part of metabolomic experiment is disintegration methods with have a big influence on the results [1], [2].

In this experiment six bacterial strains (*Pseudomonas aeruginosa, Escherichia coli, Klebsiella pneumoniae, Corynebacterium glutamicum, Bacillus cereus, Enterococcus feacalis*) were analyzed. All samples were prepared in five repetitions. For this analysis three different methods of cell disintegration were compared (sonication, sand mill and Tissue Lyser) and the methanol-water extraction method (1: 1) was chosen.

Results showed that the metabolites concentration is changing depends on used disintegration method. The sand mill proved to be the best method for two strains (*E. coli* and *E. faecalis*). Sonication proved to be the best method for three strains (*K. pneumoniae, P. aeruginosa* and *C. glutamicum*). Tissue Lyser was the best for *B. cereus*. Differences are more likely due to different cell wall structures. Results were provide also that each bacteria strain have they own metabolomic profile. PCA and OPLS models showed good grouping of different strains.

Proper disintegration method and conditions for selected material may be crucial for the experiment results. It may be very significant for samples containing different species of microorganism. These results provide that NMR (currently MS is widely used) can also be a method for identifying and distinguishing bacterial strains.

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VOLATILE PROFILING BY SPME GC-MS FOR AUTHENTICATION OF GREEN TEA (*Camellia Sinensis*) SAMPLES AND SUPPLEMENTS

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Tea, obtained by infusion of *Camellia sinensis* leaves, is the second most consumed beverage after water because of its many beneficial health properties and characteristic aroma[1,2]. Among the wide diversity of varieties used for tea infusions, those based on non-fermented green tea, and in particular matcha tea, are widely consumed and highly appreciated by consumers[3]. Moreover, an increasing number of green-tea based food supplements have recently emerged to meet the demand of natural products for overweight control. Despite a number of studies have addressed the characterization of green tea volatile composition for correlation with its sensory attributes, scarce attention has been paid to its application for determining green tea quality and authenticity.

In this work, a solid-phase microextraction (SPME)-based method has been optimised for the GC-MS analysis of volatiles in different green tea samples. Under optimal conditions (DVB/Carboxen/PDMS fiber, 0.5 g tea, T=60˚C, t_{eq}=t_{ext}=15 min), a total of 93 compounds of different functionality were identified, with 1-penten-3-ol, hexanal, 6-methyl-5-hepten-2-one, limonene, etc. showing the highest concentrations. A wide variability, probably associated to a number of factors (harvesting location, processing, quality, etc.) or their combination, was found for green tea samples and supplements based on tea leaves. SPME GC-MS analysis of intended laboratory-made adulterations evidenced that green tea and matcha tea showed a distinctive profile. 2-Ethyl-furan, α-ionone, dihydroactinidiolide and linalool oxide were identified by stepwise discriminant analysis as the most significant variables for discrimination of both green tea samples. These results are a preliminary contribution to the proposal of these volatiles as green tea/matcha tea authenticity markers.

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ANALYTICAL PLATFORM FOR THE STUDY OF PTSO METABOLIC PATHWAY

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Allium derivative propyl propane thiosulfonate (PTSO) is a new additive for animal feed which improves animal health when used as an alternative to antibiotic growth promoters. Despite the beneficial effects of the use of PTSO [1], information available on the metabolization of this new additive is sparse. This work is focused on the development of an analytical platform to elucidate PTSO metabolic pathway in rats. Specifically, gas chromatography - mass spectrometry (GC-MS) and ultra-high performance liquid chromatography quadrupole with time-of-flight mass spectrometry (UHPLC-Q-TOF) were combined with the aim of monitoring as many compounds as possible. A total of 25 rats were fed with a dose of 55 mg kg^{-1} of PTSO (single intake), which represents around 15-18 mg of PTSO per rat. In addition, other 5 rats were used as control. After PTSO ingestion, plasma and liver were collected at 0, 0.5, 2, 5, 5, 24 and 48 h, whereas urine was collected at 0, 24 and 48 h in both rat groups. For the extraction of PTSO and derivatives, two different sample treatments were developed: liquid-liquid extraction and salting-out assisted liquid–liquid extraction (SALLE) for GC-MS and UHPLC-Q-TOF analysis, respectively. The application of this analytical platform revealed the presence of propyl disulfide (PDS) derivative in liver samples of the group of rats fed with PTSO, obtaining concentrations between 0.11-0.61 µg g^{-1} and a maximum concentration at 0.5 h. PDS was present in all plasma samples with concentrations between 2.1-2.4 µg mL^{-1}, meanwhile PTSO was found at times above 5 h (0.18 µg mL^{-1}). Both compounds, PTSO and PDS, were excreted in urine from 24 h after ingestion.

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HYPHENATION AND MULTIDIMENSIONALITY AS SAMPLE PREPARATION ALLEYS IN MOSH AND MOAH ANALYSIS

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Multidimensional separation techniques are a powerful class of analytical techniques that allow to increase the separation power of complex samples, most frequently in an automated and hyphenated way. The most important parameter two optimize is the orthogonality of the separation techniques in order to maximize the overall separation. Most usually two chromatographic dimensions are coupled for this purposes (e.g., GC-GC or GC×GC, LC-GC or LC×GC, LC-LC or LC×LC), with often the addition of mass spectrometry as an extra dimension.

Few samples really benefit for additional dimensions, and mineral oil, more specifically mineral oil saturated and aromatic hydrocarbons (MOSH and MOAH) are one of this. The reference method for this analysis is the LC-GC-FID method developed by Grob and Biedermann in 2009 [1]. In this method, the LC step is used as a preliminary sample preparation step to separate MOSH and MOAH and the rest of the sample (mainly lipid components). Beside LC-GC, comprehensive gas chromatography (GC×GC) has been proposed to better investigate the identity of the MOSH and MOAH fraction.

In this work, we proposed a fully integrated platform, namely LC-GC×GC-ToFMS/FID, coupled with a novel integration algorithm, to improve results reliability. Every dimension involved was an important alley for sample preparation allowing an additional “chromatographic purification” of the MOSH and MOAH hump from the interferences still remaining after the previous LC step [2].

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QUANTIFICATION AND CHARACTERIZATION OF MINERAL OIL IN FISH FEED BY LC-GC×GC-TOFMS/FID.

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Mineral oil, mainly composed by mineral oil saturated and aromatic hydrocarbons (MOSH and MOAH), is an ubiquitous food contaminants of high concern in the European Union for it potential toxicity. Moreover, the analytical procedure for their determination is highly sample dependent and not robustly validated. High attention is devoted to human food, while often-reduced attention is paid to animal feed, turning out in higher contamination occurrence.

In this study 22 different fish feed products were selected (7 commercial feed, 5 feedstuff and 10 from sperimental diets). The analysis were performed by both LC-GC-FID as the reference method and LC-GC×GC-TOFMS/FID for confirmation of the quantity found and a more detailed characterization of the contamination [1]. The samples were first extracted by performing a microwave-assisted saponification and simultaneous extraction step, followed by an offline auxiliary technique, such as epoxidation to remove most of the interferents of the MOAH fraction and an aluminum oxide purification step when necessary on the MOSH fraction to remove overloading alkanes. The results indicate a constant contamination of MOSH ranging between 7 and 30 mg/kg and a contamination of MOAH ranging from 0.5 to 5 mg/kg.

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SUSTAINABLE MICRO-SCALE EXTRACTION OF BIOACTIVE PHENOLIC COMPOUNDS FROM *Vitis vinifera* LEAVES WITH IONIC LIQUID-BASED SURFACTANTS

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Viticulture and wine production are important agro-economic activities worldwide, with the consumption of the grapes being the main route of exploitation in this field. These processes also generate huge amounts of residues leading to an increasing demand in valorization and reuse of *Vitis vinifera* by-products. In this sense, grapevine leaves are chiefly characterized by phenolic compounds which can be exploit for numerous applications within pharmaceutical and cosmetic sectors [1,2]. Different approaches have been developed for the extraction of these natural compounds from *Vitis vinifera* by-products. These methods normally require numerous steps and large amounts of organic solvents. In this regard, this study proposes a new sustainable and simple strategy for the micro-scale extraction of phenolic compounds from grapevine leaves with analytical purpose. The method is based on a microwave-assisted solid-liquid extraction approach (MA-SLE), using an aqueous solution of an ionic liquid (IL)-based surfactant as extraction phase. ILs are a well-known alternative to conventional organic solvents due to their lower toxicity and impressive synthetic tunability. Two IL-based surfactants were evaluated, and the method was optimized by using experimental designs, resulting in the use of small amounts of sample (100 mg) and extraction phase (2.25 mL), low concentrations of the selected 1-hexadecyl-3-butyl imidazolium bromide IL (0.1 mM), and 30 min of extraction time. The method does not require organic solvents, nor any clean-up step, apart from filtration prior to the injection in the analytical system. The proposed methodology was then applied for the determination of the polyphenolic pattern of six different varieties of *Vitis vinifera* leaves from the Canary Islands, using HPLC and UV detection for the quantification of the compounds. The proposed MA-SLE approach is greener, simpler, and more effective than other methods, while the results from the analysis of the leaves samples demonstrate that these by-products can be exploited as a source of natural compounds for many applications [3].

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ENHANCING THE VOLATILE PROFILE AT SUB-AMBIENT TEMPERATURE BY USING VACUUM-ASSISTED HS-SPME. CASE STUDY ON FISH SPOILAGE.

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Headspace solid-phase microextraction (HS-SPME) is an easy, effective and selective technique for the analysis of volatiles and semi-volatiles compounds. However, long equilibration time is requested to reach optimized extraction conditions. Equilibrium is reached faster in agitating or heating the sample. Heating sample increases the extraction kinetics. However, artefact production can be a limitation, especially for matrices sensible to temperature. Beside other strategies to improve extraction kinetics, the use of vacuum has been recently and successfully proposed to speed up the extraction without increasing the temperature.

The aim of this work was to investigate and compare the use of Vac-HS-SPME to regular HS-SPME sampling from complex solid food like fish. The performances of Vac-HS-SPME were investigated at different sampling temperatures and times. In the present work, the effects of extraction temperature, sampling time and SPME phase were investigated using traditional one variable at a time approach. A series of compounds, markers of fish spoilage and covering the entire chromatogram, were selected for the comparison. Gas chromatography coupled to a single quadrupole mass spectrometry was used for the final determination.

Comparable results were obtained between sampling at 5 °C under vacuum condition and at 40 °C at atmospheric pressure. This work showed that the use of vacuum can be a powerful approach for volatiles sampling in refrigerated foods.

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EXPLORING THE CAPABILITY OF THE HISORB PROBE FOR CHARACTERIZATION OF VOLATILE AND SEMI-VOLATILE COMPOUNDS IN BREWED COFFEE BY GC×GC-QMS

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Volatile and semi-volatile components are highly relevant to characterize different samples, among which food. These compounds contribute to the peculiar aroma profile of foods and are widely used to assess quality and authenticity. The analysis of volatile and semi-volatile compounds requires the sampling of the headspace (HS) above the sample, which, now a day is mainly performed using high-concentration-capacity HS (HCC-HS) approaches, such as solid-phase microextraction (SPME), stir-bar sorptive extraction (SBSE). More recently, HiSorb has been introduced to fill the gap between SPME and SBSE. In fact, it can be easily automated (as for SPME) but present a significantly higher sorbent volume which allows a much higher trapping capacity.

The aim of this work was to exploit the potentiality of HiSorb for the analysis of volatile and semi-volatile from brew coffee and compared to the traditional triphasic SPME fiber more widely applied. Time and temperature conditions were carefully optimized, and the possibility of performing multiple cumulative trapping was investigated as well. The analyses were performed on a multidimensional comprehensive gas chromatographic system coupled with a quadrupole mass spectrometer (GC×GC-qMS) and equipped with a Flow modulator. The fingerprinting obtained from a series of different coffee was investigated for quality and authentication purposes.

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LAB-IN-SYRINGE AUTOMATED SAMPLE PREPARATION PROCEDURES BASED ON HOMOGENEOUS LIQUID-LIQUID EXTRACTION

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Two novel methods based on Lab-In-Syringe-automated homogeneous liquid-liquid extraction for the preparation of complex sample being urine and milk are presented. In both cases, the preparation procedure was coupled on-line to high performance liquid chromatography (HPLC). The procedures were carried out in the void of an automatic syringe pump integrating a magnetic stirring bar for on-demand homogenous mixing and using acetonitrile as a water-miscible extraction solvent. A saturated salt solution was then aspiarated to induce phase separation. The methodology was applied to the extraction of moderately polar sulfonamide antibiotics. Homogeneous liquid-liquid extraction enables the use of polar solvents that are compatible with separation techniques. On the other hand, the achievable preconcentration factor is limited by the need to use a solvent-sample ratio close to unity. To improve both preconcentration factor and extract clean-up, on-line solid-phase extraction (SPE) was done in addition in the first work. For this, the extract was diluted in-syringe with alkaline buffer and the analytes were trapped on an anion-exchange cartridge integrated into the HPLC injection loop. Thus, we achieved double-stage and orthogonal sample clean-up. Analytes were eluted from the cartridge by the acidic mobile phase in gradient elution mode. Running the separation of the analytes and the two-step preparation of the following sample in parallel allowed reducing the total time of analysis to 13.5 min. The method was applied to spiked urine samples yielding an average recovery of 102.7 +/- 7.4% and limits of detection at low ppb level.

In continuation, the procedure was adapted for automated and centrifugation-less deproteination of milk samples. In this case, the solvent acted both as denaturing and precipitating agent as well as for extraction. First results from this study will be presented.

Acknowledgement: The study was supported by the STARSS project (Reg. No. CZ.02.1.01/0.0/0.0/15_003/0000465) co-funded by ERDF.

LEACHING OF PAHS FROM HEAT-NOT-BURN TOBACCO PRODUCTS AND CIGARETTE BUTTS

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Conventional cigarette butts are the single most collected item in annual international coastal and urban clean-ups. Once dumped, they move through sewer systems and streams into the oceans and have a tendency to accumulate in localized areas. The cumulative effect of many littered cigarette butts may present a significant threat to local organisms as past studies have found cigarette litter toxic to some aquatic species [1]. A novel 'heat-not-burn' tobacco product was introduced that is becoming increasingly popular. However, its exposure to environmental water bodies is unknown. A limited amount of studies have been conducted regarding the quantification of leached PAHs focusing solely on the conventional cigarette butts [2-4]. The present work aims to investigate for the first time, the total and biovailable PAHs concentrations from leachates from used and unused tobacco products from heated tobacco sticks with aluminum paper (TSAl) and conventional cigarettes (CC) as well as the contribution of the different parts (i.e. filter, tobacco and paper) of TPs. The results were compared to the dissolved and total concentrations found for tobacco product entities. HiSorb sorptive extraction is used high capacity PDMS-based probes for the extraction of PAHs directly from the complex leachates. Naphthalene was proven to be the compound with the highest total and bioavailable concentrations recorded. The effects of varying pH, salt and humic acids and matrix on the leaching behavior of PAHs from TPs was also studied.

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This research was funded by an Investigator-Initiated Study award by Philip Morris Products SA (IIS.PMI.2017.30). The authors wish to thank Philip Morris Products SA for lending the machine-smoking. The authors also wish to thank Markes International Ltd for lending the thermodesorption unit (TD100-xr™) and HiSorb agitator.

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UV-254 DEGRADATION OF NICOTINE IN NATURAL WATERS AND LEACHATES PRODUCED FROM CIGARETTE BUTTS AND HEAT-NOT-BURN TOBACCO PRODUCTS

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Nicotine is an important emerging contaminant widely detected in water resources [1-3]. This study examines the UV254 photolytical fate of nicotine in natural water and leachates produced from conventional cigarettes (CCs) and the new generation heat-not-burn (HnBs) tobacco products [2]. The effect of UV254 irradiation on nicotine depletion in ultrapure water was initially studied and the effect of several parameters (pH, presence of humic acids and salts) was investigated. The chemical structures of six photo-products were derived by means of liquid and gas chromatography coupled with mass spectrometry. Leachates from used HnBs and smoked CCs were also submitted to UV254 irradiation and direct photolysis was found to proceed fast despite the high complexity of these matrices. HiSorb sorptive extraction was used as a high capacity PDMS-based probe for the extraction of nicotine directly from the leachates, coupled with TD-GC/ITMS. Finally, we take advantage of the present investigations and report the leaching behavior of nicotine from HnBs and CCs. Our findings demonstrate the importance of properly disposing tobacco product waste to prevent nicotine leaching in water bodies.

Acknowledgement: This research was funded by an Investigator-Initiated Study award by Philip Morris Products SA (IIS.PMI.2017.30). The authors wish to thank Philip Morris Products SA for lending the machine-smoking. The authors also wish to thank Markes International Ltd for lending the thermodesorption unit (TD100-xr™) and HiSorb agitator.

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LAB-MADE STIRRING EXTRACTION UNIT BASED ON CARBON NANOTUBE-MOLECULARLY IMPRINTED MONOLITHS

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A carbon nanotube-based molecularly imprinted monolithic solid was synthesized inside a new lab-made stirring extraction unit (Figure 1). The stirring unit was fabricated using a polypropylene tube pierced by an ironware. The sorbent phase (3D macroscopic monolithic solid), consisted of interconnected carbon nanotubes covered by a thin molecularly imprinted polymeric layer (MIP), was prepared by the photopolymerization of a water-in-oil (W/O) medium internal phase emulsion (40/60 w/w%). The polymerization reaction took place in the organic or external phase containing the carbon nanotubes and the monomers (cross-linker and functional monomer). Secbumeton was also added to the organic phase as a template generating the imprinted cavities, which provided selective recognition sites in the material. The non-imprinted polymers (NIPs) were prepared following the same procedure without the addition of the template. The developed units were used for the extraction of secbumeton and structurally related compounds (triazine herbicides) in peppermint mint and tea samples. A higher extraction efficiency and selectivity was achieved with the imprinting of the template in the polymeric layer (in comparison with the NIP). The limits of detection (LODs) were between 0.4 and 2.5 µg·L^{-1}. The intra- and inter-day precision of the method was also evaluated as relative standard deviation, observing values which ranged from 3% to 9% and 9% to 15%, respectively.

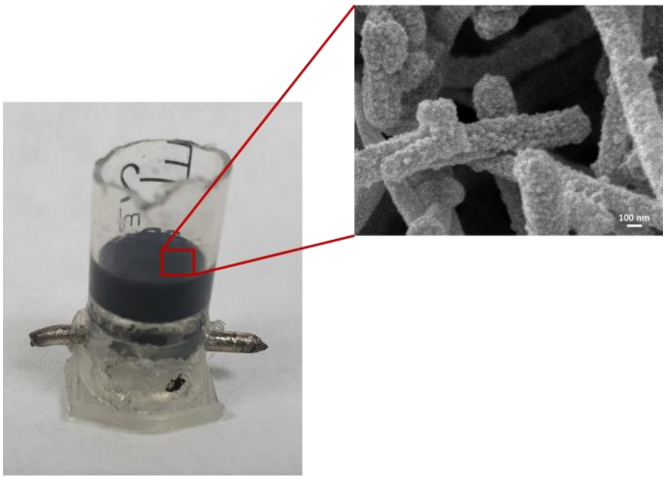

Figure 1. Photography of the lab-made stirring extraction unit and SEM micrograph of the carbon nanotube-based molecularly imprinted monolith.

MAGNETIC SOLIDS BASED ON CARBON NANOTUBES PREPARED FROM PICKERING EMULSIONS

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Two types of magnetic solids based mainly on carbon nanotubes, such as monolithic solids and spherical microparticles, have been synthesized by photopolymerization emulsion templating. Water-in-oil (W/O) and oil-in-water (O/W) Pickering emulsions were used selecting polystyrene-modified magnetic nanoparticles as stabilizers. It should be highlighted that using polystyrene-modified magnetic nanoparticles as stabilizers in water/chloroform mixtures, stable W/O and O/W Pickering emulsions can be achieved being possible to continuously switch from one to other. In addition to this, magnetic nanoparticles provided magnetic response to the obtained solids in the presence of an external magnetic field fulfilling thus a double mission. On the other hand, the incorporation of carbon nanotubes was equally significant, because without them the polymerization reaction was not successfully completed. The two types of Pickering emulsions led to structurally different final solids despite being formed by the same components. On one hand, W/O Pickering emulsions produced monolithic solids. On the other hand, O/W Pickering emulsions formed spherical magnetic microparticles. The morphology of both magnetic solids containing carbon nanotubes was characterized by scanning electron microscopy (SEM). Finally, a comparison between the extraction efficiency of magnetic monolithic solids and microparticles was carried out using polycyclic aromatic hydrocarbons as target analytes. The best results were obtained with the magnetic microparticles obtaining limits of detection (LODs) between 1 and 4 $\mu g \cdot L^{-1}$ and excellent recovery values (99-108 %) in chamomile tea samples.

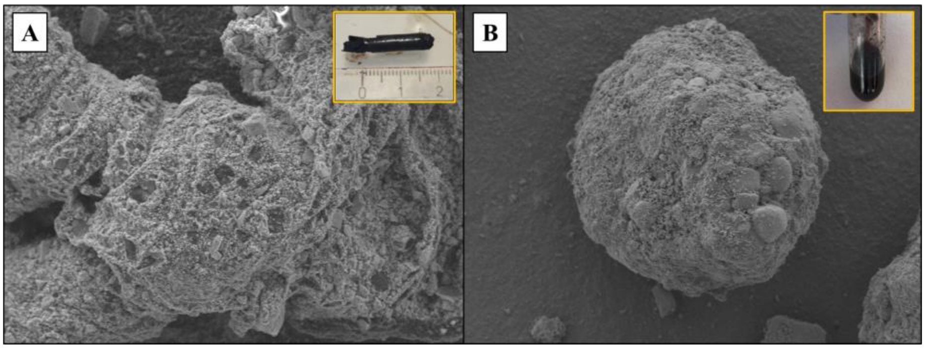

Figure 1. Photographs and SEM micrographs of the magnetic solid based on carbon nanotubes prepared from A) W/O and B) O/W Pickering emulsions.

DEVELOPMENT AND VALIDATION OF METHODS USING SOLID-PHASE EXTRACTION, OFFLINE DERIVATIZATION AND UHPLC-ESI(+)-MS/MS FOR THE QUANTIFICATION OF ESTROGENIC COMPOUNDS AT ULTRA-TRACE LEVELS IN DIFFERENT TYPES OF WATER

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Natural estrogens (estrone: E1, 17-β-estradiol: E2, estriol: E3) and synthetic estrogen (17-α-ethinylestradiol: EE2) belong to the group of endocrine disrupting compounds (EDCs), leading to deleterious effects on aquatic biota, even at sub-ng/L level of concentration. The European Union (EU) published a Watch-List of substances including these estrogenic compounds and specified maximum acceptable method detection limits (LODs) of 0.035 ng/L for EE2 and 0.4 ng/L for E1 and E2. Besides, E2 will have to be monitored as an indicator of the occurrence of EDCs in water intended for human consumption, with a parametric value of 1 ng/L (EU 2020/2184). Attaining these limits represents a challenge even with the most up-to-date analytical tools, particularly in surface water. Initially, an automated solid-phase extraction (SPE) method using a single cartridge with hydrophilic-lipophilic balanced copolymer was developed and validated. This method is suitable for clean aqueous matrices (drinking water) and allows for high sample throughput. However, for more complex matrices such as surface water/effluent of wastewater treatment plant, an additional purification step was necessary. After a careful optimization of the sample preparation parameters to maximize the recoveries, the extraction of a whole water sample on a SPE disk, followed by purification on a Florisil SPE cartridge, allowed to reach the sensitivity required by the EU Watch-List. The final optimized method was validated (precision and trueness) in seven surface water from different Belgium locations.

COMPUTER FAN'S POTENTIAL IN AIR SAMPLING

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Air sampling is challenging due to the low concentration of the target analytes and the heterogeneity (spatial and temporal) of this environmental compartment. The acquisition of large volumes of air samples is therefore required to guarantee the sensitivity of the determinations and the representativeness of the sample [1]. The design and validation of new devices which integrate sampling and preconcentration in one step are crucial for environmental air analysis [2]. These devices can be active or passive samplers taking advantage of the versatility derived from solid-phase microextraction (SPME) [3].

In this communication a new air sampling device based on a computer fan (Figure 1), supporting the sorbent fabric phase (FP) on its blades, is presented. The FP location is critical, and the FP must be placed where the interaction with the air flow is maximum. This device was used to extract volatile organic compounds from air in a laboratory environment. Furthermore, the potential to isolate biogenic volatile compounds from solid natural samples was demonstrated [4].

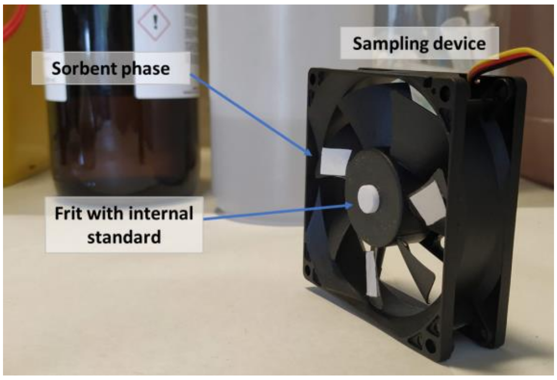

Figure 1. Fan based air sampling device.

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COMPOSITES BASED ON METAL-ORGANIC FRAMEWORKS AND THEIR POTENTIAL APPLICATION IN DISPERSIVE MICRO-SOLID-PHASE EXTRACTION

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The miniaturization of conventional extraction methods has represented a significant advance for sample preparation, leading to the reduction of its environmental impact without compromising the quality of the results intended for any analytical method. Likewise, the rise of these methodologies has implied an unavoidable convergence between Analytical Chemistry and Materials Science through the incorporation of new materials, such as metal-organic frameworks (MOFs). MOFs are highly ordered polymeric crystalline three-dimensional structures constituted by metallic ions (or clusters) and organic ligands connected through coordination bonds. These polymeric frameworks are characterized by having cavities and regular pores that provide high surface areas. Furthermore, MOFs have great synthetic and structural versatility due to the endless number of possible metal-ligand combinations, allowing even post-synthetic modifications. Currently, the employment of MOFs-based composites has attracted considerable interest in the field of Analytical Chemistry owing to the inclusion of synergistic effects from the different materials (silica, polystyrene, …) and the MOF to provide superior materials. In this study, we propose the preparation and evaluation of different composites based on MOFs for their potential use in dispersive micro-solid-phase extraction (μ-dSPE).

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FABRIC PHASE SORPTIVE EXTRACTION OF SELECTED POLYCYCLIC AROMATIC HYDROCARBONS FROM HERBAL INFUSIONS AND TEA SAMPLES FOLLOWED BY ANALYSIS USING GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Food is among the major sources of human exposure to polycyclic aromatic hydrocarbons (PAHs), which are persistent pollutants that can be present in various foods including fruit, vegetables, meat, fish, milk and beverages [1]. PAHs exist in environmental samples and they might accumulate in tea plants, while the processing of the tea sample s (i.e., drying and heating) may result in contamination with PAHs [2]. This study presents the development of a fabric phase sorptive extraction (FPSE) method for the extraction of selected PAHs from herbal infusions and tea samples prior to their analysis by gas chromatography-mass spectrometry (GC-MS). For this purpose, various sol-gel coated FPSE membranes were evaluated. Among the different examined FPSE membranes, best performance was observed using the sol–gel C_{18} coated FPSE membrane. The detection limits were 0.08-0.17 ng mL^{-1} and the quantification limits were 0.25-0.50 ng mL^{-1}. Moreover, the relative standard deviation was less than 7.9% for intra-day and less than 8.5% for inter-day repeatability. The method was successfully applied for the determination of PAHs in a wide variety of herbal infusions and tea samples demonstrating good accuracy, since the relative recoveries of the selected PAHs ranged between 91.9% and 109.8%. Finally, the proposed sol-gel C_{18} coated FPSE membranes were found reusable for at least 5 times.

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A MONOLITHIC CAPSULE PHASE MICROEXTRACTION PLATFORM COMBINED WITH HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-DIODE ARRAY DETECTION FOR THE MONITORING OF TRIAZINE HERBICIDES IN WATER SAMPLES

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Triazine herbicides are a group of widely used pesticides that can be dangerous both for humans and for the aquatic environment due to their inherent high toxicity and endocrine disrupting effect of their members [1,2]. Therefore, the determination of triazine herbicides in water samples is of high importance. Capsule phase microextraction (CPME) is a novel extraction technique that utilizes powerful sol-gel sorbents. CPME integrates the filtration and stirring mechanism into one extraction device. In this study, monolithic sol-gel Carbowax 20 M capsules were used for the extraction of six triazine herbicides (i.e., simazine, cyanazine, atrazine, prometryn, terbuthylazine and propazine) from water samples prior to their determination by high performance liquid chromatography-diode array detection (HPLC-DAD). The main parameters affecting the adsorption (e.g., adsorption time, sample volume, stirring rate, ionic strength) and desorption steps (e.g., type of eluent, desorption time and elution volume) of CPME procedure were investigated and optimized. The limits of detection were 0.15 ng mL^{-1}. Furthermore, the relative standard deviation for the within-day and between-days repeatability were less than 7.2% and 9.9%, respectively. Finally, the method was successfully employed for the analysis of mineral water, tap water, rainwater, and lake water samples.

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A SOL-GEL ZWITTERIONIC MIXED-MODE PLATFORM FOR THE FABRIC PHASE SORPTIVE EXTRACTION OF TRIAZINE HERBICIDES FROM FRUIT JUICE SAMPLES

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Triazine herbicides are a class of common pesticides used to control the weeds in many agricultural crops [1]. Although many studies have described methods for the determination of these analytes in environmental samples, the attention given to agricultural crops and similar matrices is limited [2]. In this study, a novel sol-gel zwitterionic mixed-mode platform was synthesized and used for the fabric phase sorptive extraction (FPSE) of simazine, atrazine, prometryn, terbuthylazine and propazine from various fruit juices followed by their determination by high performance liquid chromatography-diode array detection (HPLC-DAD). The main parameters affecting the adsorption and elution of the target analytes were investigated and optimized. Under the optimum conditions, the limits of detection were 0.15 ng mL^{-1} and the limits of quantification for the target analytes were 0.50 ng mL^{-1}. The relative standard deviation for the intra-day repeatability and for inter-day precision were less than 5.6% less than 8.8% respectively. The proposed method was successfully employed for the analysis of fruit juice samples demonstrating good accuracy.

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MAGNETICALLY INTEGRATED FABRIC PHASE SORPTIVE EXTRACTION OF SELECTED ENDOCRINE DISRUPTING CHEMICALS FROM HUMAN URINE PRIOR TO HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY – PHOTODIODE ARRAY ANALYSIS

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Endocrine disrupting chemicals (EDCs) are primarily synthetic and secondarily natural chemical substances, which disrupt the phycological function of the endocrine hormonal systems. [1] The esters of p-hydroxybenzoic acid, wider known as parabens, and Bisphenol A are well-recognized EDCs. The bioanalysis of parabens and BPA is a matter of ongoing interest. Generally, sample preparation is a fundamental part of any bioanalytical method due to the matrix complexity. Currently, the integration of different processes that are the key contributions for the selective extraction of the target analytes is a very interesting concept in green sample preparation. Keeping this in mind and considering the beneficial role of stirring in the equilibrium extraction, the integrating of the extraction sorbent material unit and stirring into the same device seem to be a new advancement. [2] Herein, a new extraction/stirring integrated approach, namely the magnetically integrated fabric phase sorptive extraction (MI-FPSE) for the extraction of selected very common EDCs from human urine is applied for the first time prior to their determination with by high performance liquid chromatography-diode array analysis. The developed sample preparation approach was thoroughly studied and optimized. The proposed method performed satisfactory analytical figures of merit since the limits of quantitation were 1 ng/mL and the RSD% were lower than 9 % and was successfully applied for the analysis of real samples.

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MICROWAVE ASSISTED EXTRACTION AS A PROMISING TECHNIQUE FOR EXTRACTION OF BIOACTIVE CARBOHYDRATES FROM VEGETABLE BY-PRODUCTS

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In order to overcome major shortcomings of conventional solid-liquid extraction (SLE), mainly associated with the use of high temperatures and extended extraction times, low efficiency, etc., microwave-assisted extraction (MAE) has emerged for improved green extraction of bioactive compounds [1]. A more homogeneous heating is achieved in MAE, which allows the breakage of cells and favours the release of bioactive compounds, improving extraction yields and reducing time and solvent volume. Despite these advantages, MAE has been scarcely applied to the extraction of bioactive carbohydrates. Therefore, the objective of this work is to highlight the potential of MAE for the extraction of bioactive carbohydrates, such as inositols and prebiotic oligosaccharides, which can be abundantly found in vegetable by-products derived from agricultural practices and food industries (artichoke leaves, legume pods, vegetable waste, etc.). A closed vessel microwave system MARS6 (CEM, NC, US) provided with an optic fiber (MTS-300, CEM) for temperature control was used for the extraction. Microwave power was set at 1200 W, while a Box-Behnken experimental design was used to evaluate the effect of three independent factors (extraction temperature (T, °C); time (t, min); and solvent composition (s, % ethanol)) on extraction of carbohydrates. Finally, a response surface methodology was employed to simultaneously maximize the concentration of bioactive carbohydrates and minimize the extraction of interfering sugars. This strategy allowed to obtain extracts rich in bioactive carbohydrates from different by-products using green and food grade solvents (water/ethanol), with good efficiencies and extractions times (3-30 min) much shorter than SLE. The green methodology developed could be a promising alternative to conventional extraction for revalorization of agro-food by-products within a Circular Economy context.

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A POLY(METHACRYLIC ACID-ETHYLENE GLYCOL DIMETHACRYLATE) MAGNETIC COMPOSITE FOR TRACE DETERMINATION OF TRICYCLIC ANTIDEPRESSANTS AND THEIR ACTIVE METABOLITES IN HUMAN URINE BY STIR BAR SORPTIVE DISPERSIVE MICROEXTRACTION

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Tricyclic antidepressants (TCAs) are a group of psychoactive drugs which are used for the treatment of depression and other mental disorders. Despite these drugs have been replaced by new classes of antidepressants due to their side effects, they are still being routinely prescribed for the treatment of anxiety, eating disorders and attention deficit hyperactivity disorder, among others [1]. As a result of the narrow safety window of TCAs and the poor compliance of patients with depression, the development of sensitive and selective analytical methods for their determination at trace levels in biological samples is needed to ensure the safety of users. The aim of this work is to determine the content of five TCAs and their active metabolites in human urine samples. For this purpose, the stir bar sorptive dispersive microextraction (SBSDME) technique, developed by our research group few years ago [2,3], is employed as clean-up and preconcentration technique prior to liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis. In this case, the extraction is carried out using a composite made of $CoFe_2O_4$ magnetic nanoparticles coated with poly(methacrylic acid-ethylene glycol methacrylate) copolymer, which exhibits an excellent interaction with the target analytes. The main parameters involved in the extraction (i.e., amount of sorbent, extraction time, pH and ionic strength) and desorption (i.e., solvent and desorption time) procedures were optimized.

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TRACE DETERMINATION OF TETRAHYDROCANNABINOL (THC) IN COSMETIC PRODUCTS BY STIR BAR SORPTIVE DISPERSIVE MICROEXTRACTION-LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY

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Δ-9-tetrahydrocannabinol (THC) is a widely known psychoactive substance coming from hemp plant (*Cannabis sativa L.*) that can be present as impurity of cannabidiol (CBD), whose use in cosmetic products have expanded in the last years [1]. According to the EU Regulation, the presence of any narcotic substance is prohibited in cosmetics [2]. However, traces of THC might be present in personal care products either by contamination during the treatment of the raw material (e.g., *Cannabis sativa* seed oil) or by isomerization of CBD [3]. In this sense, the analysis of THC in cosmetic products containing CBD or hemp extracts is of great interest. Due to the complexity of cosmetic matrices and the low concentrations expected for the analyte, a sample preparation step is required. Given these circumstances, stir bar sorptive dispersive microextraction (SBSDME) [4], developed by our research group a few years ago, is proposed for sample cleanup and preconcentration of the analyte followed by a sensitive determination by liquid chromatography-tandem mass spectrometry. A composite made of $CoFe_2O_4$ magnetic nanoparticles embedded into a commercial pyrrolidine-modified styrene-divinylbenzene copolymer (Strata-X^{TM} RP) was used as sorbent material. The main parameters involved in the extraction procedure (i.e., sorbent amount, extraction time, pH and ionic strength) were evaluated and optimized using a Response Surface Methodology.

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PROFILING NAPHTHENIC ACIDS IN PRODUCED WATER USING HOLLOW FIBER LIQUID-PHASE MICROEXTRACTION COMBINED WITH GAS CHROMATOGRAPHY COUPLED TO FOURIER TRANSFORM ORBITRAP MASS SPECTROMETRY

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The oil extraction process generates the produced water (PW) as its main by-product [1]. It consists of a complex mixture of organic and inorganic compounds. Naphthenic acids (NAs) are naturally present in PW and it can be toxic and recalcitrant, causing negative effects to the environment and human health [2]. Therefore, there is a need of minitoring these compound in PW samples. Consolidated extraction techniques such as liquid-liquid extraction (LLE) and solid phase extraction (SPE) have already been employed for the extraction of NAs; however, these techniques are time-consuming and require the use of high amounts of organic solvent. In this study, we describe the development of an analytical method to isolate NAs from PW using hollow fiber liquid-phase microextraction (HF-LPME). A microwave-assisted methylation method was used to convert the free acids into its corresponding naphthenic methyl esters (NAMEs), in which the best reaction conditions were established using a central composite design. The optimized sample preparation method exhibited an improved analytical eco-scale value (80 vs. 61) compared to LLE. Although the primary goal was qualitative analysis of NAMEs (e.g., group-type separation), the quantitative performance was also evaluated for future investigations. The instrumental detection and quantification limits were 0.10 ng mL^{-1} and 0.16 ng mL^{-1}, respectively, using full spectrum data acquisition. The accuracy and precision of the proposed method ranged from 90.4 to 96.6 % and 3 to 13 %, respectively, using matrix-matched working solutions (0.1, 0.5, and 1.0 µg mL^{-1}). The group-type analysis using the monoisotopic masses of the adduct ions ($[M+H]^+$) and its corresponding isotopic patterns were used to determine the elemental composition of the NAMEs in the PW samples. Qualitative analysis indicated the O_2 class as the predominant class in all samples with carbon numbers ranging from C_5 to C_{19} and double bond equivalent (DBE) values of 1 to 8.

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MODIFIED MAGNETIC-BASED SOLVENT ASSISTED DISPERSIVE SOLID-PHASE EXTRACTION FOR THE DETERMINATION OF CORTISOL AND CORTISONE IN HUMAN SALIVA

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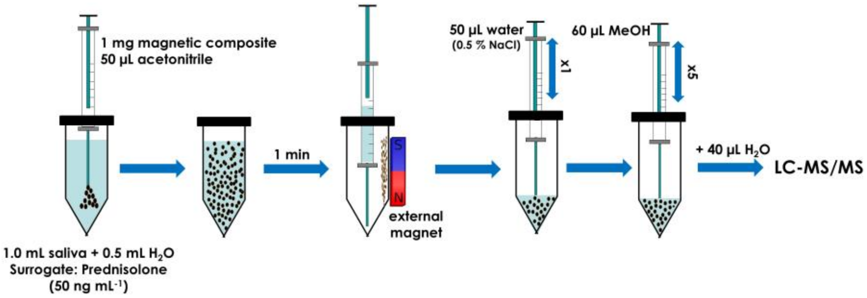
A modification of magnetic-based solvent assisted dispersive solid-phase extraction (M-SA-DSPE) [1,2] is presented. This modification imitates the conventional dispersive liquid-liquid microextraction, but employing a magnetic material as sorbent. Thus, the magnetic sorbent is quickly dispersed in the sample by means of a disperser solvent (i.e. acetonitrile). After the extraction, the sorbent retaining the analytes is retrieved by terms of an external magnet and desorbed in a small amount of organic solvent. In order to prove the analytical benefits of this modification, the determination of cortisol and cortisone in saliva has been performed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) . It should be said that salivary cortisol and cortisone have gained interest in the recent years over serum cortisol because the collection method for saliva is less invasive, furthermore they show good correlation with serum cortisol. Moreover, simultaneous determination of salivary cortisol and cortisone provides information about the malfunction of adrenal gland and Cushing's syndrome. This method has been successfully applied to human saliva from different volunteers, obtaining good recovery values (86-111 %) with low RSDs (< 10 %) and LODs of 0.029 ng mL^{-1} for cortisol and 0.018 ng mL^{-1} for cortisone.



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IN-DEPTH EVALUATION OF METAL-ORGANIC FRAMEWORKS AS SORBENTS IN ANALYTICAL MICROEXTRACTION: ADSORPTION AND KINETIC STUDIES

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Sorbent-based microextraction techniques are the most widely used analytical sample preparation approaches within a miniaturization perspective. In particular, the dispersive micro-solid-phase extraction (µ-dSPE) stands out due to its simplicity, short extraction times, and high extraction recoveries obtained by taking advantage of the direct (and efficient) dispersion of the sorbent into the sample matrix. Advances within µ-dSPE are shifted to the incorporation of new sorbent materials, which is a challenging but hot topic research line [1].

Among these new sorbents, metal-organic frameworks (MOFs) deserve highlighting. MOFs are crystalline three-dimensional materials formed by the combination of metallic ions (or clusters) with organic linkers through coordination bonds. They exhibit the highest surface areas known so far, as well as high mechanical and thermal stability, uniform porosity, and ultra-low crystal densities.

Over the last few years, the use of MOFs in µ-dSPE has become popular for the extraction of contaminants in different samples. However, despite the success of the applications reported, few studies have evaluated the nature of analyte-MOF interactions [2]. The rationale design of MOFs is highly advisable to improve their extraction ability and selectivity, and should be accompanied by proper adsorption capacity studies.

The present study evaluates both adsorption and kinetic capacities of MIL- and PCN-like MOFs, using personal care products as target analytes, intending the incorporation of these materials as sorbents in selective µ-dSPE approaches.

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OPTIMIZATION OF VAC-HSSPME+GC–MS FOR DETERMINATION OF BIOMARKER PROFILES ON OIL SOURCE ROCKS USING MULTIVARIATE APPROACHES

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The evaluation of oil source rocks depends on the characterization of the organic matter present on samples; some compounds can be assigned as biomarkers and associated to properties of the oil relevant to their potential commercial value. These compounds (mainly C_{20+} hydrocarbons found in trace amounts) are structurally similar to natural products present on the organisms that originated the oil and are formed from their diagenetic alteration. Usual procedures involve lengthy and cumbersome demanding extraction steps as Soxhlet extraction, TLC and open-column liquid chromatography before GC-MS(/MS) analysis. We propose here the combination of Vaccuum-assisted Headspace SPME (Vac-HSSPME) and GC-MS to simplify and speed up the process. This is not a mere straightforward replacement: the target compounds have very low vapor pressures (~10^{-7} bar or less) and are not analytes typically isolated using headspace manipulation procedures. A Vac-HSSPME+GC-MS procedure was optimized using rock samples collected from stratigraphic exploratory oil wells using experiments arranged according to a Doehlert design matrix. The evaluated response was total peak area for the steranes monitored through GC–MS on SIM (m/z = 217). The algorithm for the factorial planning (model fitting and generation of response surface) plots was implemented on MATLAB®. The optimum operation conditions were found to be 15 min extraction und temperature of 250 °C, using a 7 µm PDMS SPME fiber. The results for selected samples were compared to those obtained using conventional Soxhlet extraction and found to be comparable. Apart from the steranes, other relevant biomarkers compounds were identified, such as C_{27} (13β, 17α, (20S) diasterane) among others. The procedure was also validated for quantitation of these compounds, showing better sensitivity and sensibility when compared to the traditional Soxhlet procedure.

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P30

DISPERSIVE LIQUID-LIQUID MICROEXTRACTION FOR SIMULTANEOUS DETERMINATION OF MALONDIALDEHYDE, ACROLEIN AND 4-HIDROXY-2- NONENAL IN BEVERAGES BY GC-MS

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Beer, tea, coffee, and fruit juice are the most popular beverages worldwide with high phenolic content, including flavonoids and caffein. High temperatures and radiation during processing may destroy these compounds, causing the oxidation of their fatty acid content which may affect their organoleptic properties and reduce their nutritional value [1,2].

Malondialdehyde (MDA), acrolein (ARCL), and 4-hydroxy-2-nonenal (4-HNE) are secondary, more stable, peroxidation products recently used as markers of oxidative state in food. The European Food Safety Authority (EFSA) proposed a threshold of toxicological concern (TTC) at the level of 30 µg kg^{-1} of bw day-1 for MDA and 1.5 µg kg^{-1} of bw day-1 for 4-HNE. The World Health Organization (WHO) working group estimated the tolerable daily intake (TDI) of acrolein as 7.5 µg kg^{-1} of bw. [3-4]

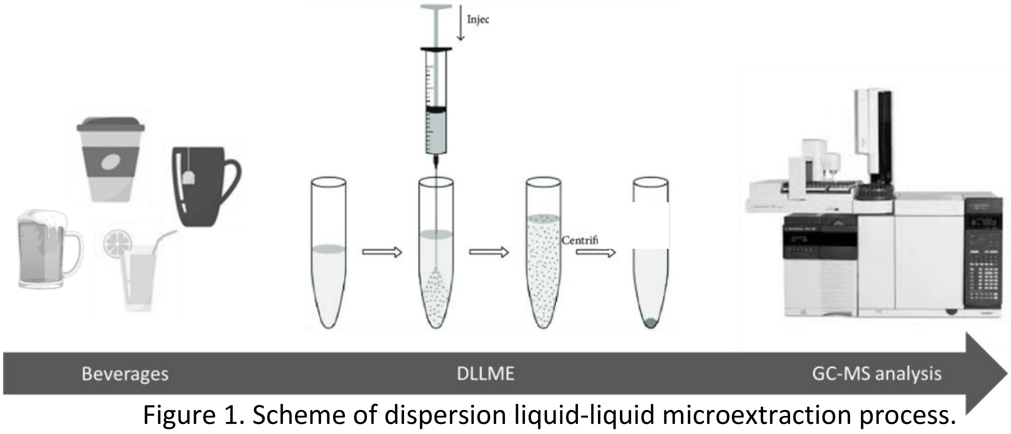

Figure 1. Scheme of dispersion liquid-liquid microextraction process.

A new DLLME protocol for the simultaneous determination of MDA, ACRL, and 4-HNE in beverages by GC-MS has been successfully developed and validated, following the Food and Drug Administration guidelines of analytical method validation [5] achieving great results.

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DEVELOPMENT AND APPLICATION OF A MINIATURIZED ACTIVE AIR SAMPLING METHOD FOR INDOOR AND OUTDOOR PLACES ADJANCENT TO SURFACES MADE OF TIRE RUBBER

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Tire rubber is a material which is reused to manufacture sport and leisure facilities. This material contains toxic substances, so its use in sport and recreational activities represents a risk to human health since one of the main routes of exposure is inhalation [1]. For this reason, a fast and simple active air sampling methodology to determine forty-one organic compounds in air adjacent to these surfaces has been developed [2]. Target compounds were selected according to previous studies on artificial turf football fields and children´s playing surfaces [3], including polycyclic aromatic hydrocarbons, plasticizers, antioxidants and vulcanization additives. The method was based on solid phase extraction followed by an extraction step (ultrasounds or vortex) with a subsequent analysis by gas chromatography-tandem mass spectrometry. To optimize the retention and the extraction of the compounds, a factorial experimental design was performed. Breakthrough volume was also studied. The method was validated in terms of linearity, precision and accuracy obtaining satisfactory results. Finally, air samples from outdoor and indoor places were analyzed, including a synthetic turf football field. In addition, the suitability of solid phase microextraction was evaluated as extraction technique.

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DETERMINATION OF FUNGICIDES IN SEVERAL MATRICES BY DIFFERENT EXTRACTION TECHNIQUES

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Fungicides are a type of pesticides used to inhibit fungal growth that can seriously damage crops [1]. Although their use is indispensable for food security, there are concerns about the presence of their residues in crops and in different environment compartments (waters, soils, etc). This can represent a health hazard to the consumers and a risk for the environment [2,3]. For this reason, this research was focused on the determination of widespread fungicides employing gas chromatography coupled to tandem mass spectrometry (GC-MS/MS) in different matrices such as leaves (vine leaves and tea), soil and grapes. For leaves analysis, ultrasound assisted extraction (UAE) was performed evaluating different solvents, and it was studied the possibility of a subsequent extraction by solid phase microextraction (SPME), optimizing the extraction mode and fibre coating. Besides, it was compared UAE with other extraction techniques as vortex and microwave assisted extraction (MAE). Regarding the other matrices, soils were analyzed by UAE and MAE, and grapes by matrix solid phase dispersion (MSPD) evaluating different drying agents.

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SYNTHESIS AND CHARACTERIZATION OF ZWITTERIONIC POLYMERIC IONIC LIQUID SORBENT FOR FIBER-IN-TUBE SPME TANDEM MASS SPECTROMETRY TO DETERMINE ALZHEIMER’S DISEASE BIOMARKER

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Fiber-in-tube solid phase microextraction (fiber-in-tube SPME) directly coupled to tandem mass spectrometry (fiber-in-tube SPME) highlights a promising on-line chromatographic system to determine non-volatile and thermally-labile compounds. This on-line system not only favors the accuracy and precision, but also reduces the analysis time and costs. Using this technique, the analytes are extracted in a short capillary that is longitudinally packed with fine fibers as the extraction medium [1]. The fiber-in-tube SPME method exhibits higher extraction efficiency, longer lifetime (reusability), and reduced pressure drop. In this study, selective zwitterionic polymeric ionic liquid and dicationic polymeric ionic liquid monomers, namely, 1-vinyl-3-(butylsulfonate)imidazolium ([$VIm^+C_4SO_3^-$]) and 1,12-Di(3-vinylimidazolium)dodecane bromide ([$(VIm)_2C_{12}$]2[Br]) were synthesized through the S_N2 mechanism. These monomers were polymerized (in-situ by a thermally initiated process) onto nitinol wires. The surface roughness (evaluated by atomic force microscopy analysis) of the nitinol wires decreased after the in-situ polymerization. Also, the success of in-situ polymerization was also confirmed by scanning electron microscopy analysis. The modified nitinol wires were packed into a PEEK tube and the extractions directly coupled with tandem mass spectrometry (MS/MS) to determine amyloid β peptides (Alzheimer’s disease biomarker) in cerebrospinal fluid sample. The fiber-in-tube SPME-MS/MS method was fully optimized and the highest extraction recovery was achieved using the following conditions: preconcentration/cleanup with 0.3% formic acid at 0.1 µL min^{-1}, and elution with 20:80 water:acetonitrile (with 0.3% ammonium hydroxide v/v) during 5 min. Based on obtained results, the analytes were preconcentrated through a combination of ion exchange and dipole-dipole interactions. Future studies will consist of analytical validation and application of the fiber-in-tube SPME-MS/MS method to determine amyloid β peptides in biological fluid obtained from patients with Alzheimer’s Disease.

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SYNTHESIS AND CHARACTERIZATION OF A MONOLITHIC STATIONARY PHASE WITH SULFONIC GROUPS FOR IN-TUBE SPME-LC-MS/MS TO DETERMINE AMYLOID BETA PEPTIDES IN BIOLOGICAL SAMPLES OBTAINED FROM PATIENTS WITH ALZHEIMER'S DISEASE

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Alzheimer's Disease (AD) is characterized by substantial neuronal loss and progressive brain atrophy. Biomarker studies based on biological matrixes such as cerebrospinal fluid and plasma represent the most direct means to study AD progression and to detect the AD preclinical and symptomatic stages. Sample preparation of biological matrixes is an important step during the development of LC-MS/MS methods: it removes endogenous macromolecules and pre-concentrates trace-level analytes. In this context, in-tube solid phase microextraction (in-tube SPME) has emerged as an effective on-line sample preparation technique that allows hyphenation of the sample preparation step with chromatographic analysis, thereby improving analytical sensitivity and selectivity [1].

In this study, a monolithic stationary phase with sulfonic groups was synthetized (in-situ polymerization) in the inner surface of a fused-silica capillary for use in the first dimension of the in-tube SPME-LC-MS/MS system. Optimum synthesis reaction conditions were: 60 °C for 24 h, 1-propanol and water as solvents, 3-sulfopropyl methacrylate potassium salt as functional monomer, ethylene dimethacrylate as crosslinker, and 2,2'-azobis(2-methylpropionitrile) as radical initiator. The final monolithic stationary phase was characterized by Scanning Electron Microscopy (SEM).

The in-tube SPME method was optimized to establish the best extraction conditions: preconcentration and cleanup steps with water for 2 min and 5 min, respectively, and elution step with water and acetonitrile (with 0.3% ammonium hydroxide in both, 20:80 v/v) for 6 min. The LC-MS/MS conditions were: BEH C18 peptide column (150 mm × 2.1 mm, 1.7 µm) at 35 °C and mobile phase consisting of water (0.3% ammonium hydroxide) and acetonitrile (90:10, v/v) at a flow rate of 0.2 mL min^{-1} and elution in the gradient mode. Future steps will include analytical validation and application of the in-tube SPME-LC-MS/MS method to determine amyloid beta peptides in biological samples obtained from patients with Alzheimer's Disease.

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DEVELOPMENT AND VALIDATION OF ANALYTICAL METHOD BASED ON MINIATURIZED MATRIX SOLID-PHASE DISPERSION FOR DETERMINATION OF PHTHALATES (PHTs) IN MUSSEL

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Phthalates (PHTs) are widely used as plasticisers in the processing of plastic products and in the manufacturing of cosmetics, propellants and insecticides, this makes them the most ubiquitous compounds in the environment and the food chain. PHTs reach the marine ecosystems by wastewater and riverine inputs. Different mixtures are used in industry in order to provide plastics with a wide range of properties as flexibility, transparency and longevity. Six phthalates have been included as priority pollutants of the European Union (dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), benzyl butyl phthalate (BzBP), diethyl hexyl phthalate (DEHP) and di-n-octyl phthalate (DnOP)). A number of studies have shown the significant effects of PHTs on the reproduction of marine organisms [1], but the risk assessment of only certain phthalates has been studied, so it is necessary to monitor their occurrence in the marine environment and food chain.

A miniaturized methodology based on matrix solid phase dispersion (μ-MSPD) applied to the analysis of the six priority phthalates (DMP, DEP, DBP, BzBP, DEHP and DnOP) in mussel was developed. This approach allows performing the extraction and clean up of sample at the same step, then extracts were quickly determined by Gas Chromatography-Mass Spectrometry in tandem (GC-MS/MS). This procedure leads to an inexpensive, rapid and easy method, very appropriate for monitoring laboratories. The extraction and clean up conditions (parameters), amount of sample, dispersant agents A (Florisil dispersed with sample before column) and B (Florisil in column), and extractant volume, were optimized using a fractional factorial design 2^{5-1}. Except for DBP extraction, all compounds had some statistically significant parameter. The analytical performance demonstrated recoveries around 90% and relative standard deviation below 10%. The analytical method was applied to the analysis of several mussel samples (*Mytilus galloprovincialis*) from the estuarine bays (Rías) in Galicia coast (NW, Spain).

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MULTI-RESIDUAL APPROACH FOR THE DETERMINATION OF BPA AND ITS SUBSTITUTES IN WATER AND SOFT DRINKS

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Bisphenol A (BPA) is a well-known endocrine-disrupting compound (EDC) whose use is regulated [1] and, in some cases, restricted [2] by the European Union. Due to these actions, manufacturers are switching to other substitutes, with a similar structure to BPA, to be used in different applications, such as bisphenol B (BPB), bisphenol F (BPF), bisphenol S (BPS), bisphenol AF (BPAF), fluorene-9-bisphenol (BHPF), bisphenol Z (BPZ) and tetramethyl bisphenol F (TMBPF). However, several studies have demonstrated that all of them also exhibit endocrine-disrupting properties [3]. Within a regular diet, fluid intake is one of the most important factors for correct hydration and healthy state of the individual, being water and soft drinks the greatest contributors of fluids through the diet for the adult population [4]. Therefore, these drinks have special relevance in studies on estimating the intake of EDCs from food contact materials (FCMs) such as cans and plastic bottles. For all these reasons, it is necessary to develop analytical protocols that allow the multi-residue determination of BPA and its substitutes in water and soft drinks usually consumed by the general population. A fast and multi-residue method based on ultra-high performance liquid chromatography coupled to triple-quadrupole mass spectrometry (UHPLC-QqQ) has been optimized and characterized in terms of linearity, precision and limit of detection and quantification. Besides, different solid-phase extraction (SPE) conditions have been tested to achieve the quantitative extraction of the eight-targeted bisphenols in water and soft drink samples.

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CLASSIFICATION OF OLIVE OIL QUALITY AND GEOGRAPHICAL ORIGIN BY USING A MULTI-CUMULATIVE TRAPPING HS-SPME-GC-MS FOLLOW BY A NOVEL DATA HANDLING SOFTWARE

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The sensory attributes of extra virgin olive oil, and in particular specific aroma defects, are officially responsible for oil classification (or declassification) into extra virgin, virgin or lampante olive oil. Undoubtedly, volatile compounds play a crucial role in defining olive oil sensory quality and research efforts have been dedicated to unravel the composition of this informative fraction, to better understand correlations with quality attributes. The relative distribution of volatiles depends on several parameters (i.e., cultivar, geographical origin, fruit ripeness, processing practices, and storage) meaning the identification of an unequivocal fingerprint correlated to quality and authenticity is a difficult task. Most of these variables contribute towards the intensity and quality of the green and fruity perception, while the presence of defects is mainly due to inappropriate manufacturing practices.

Multiple-cumulative trapping headspace-solid-phase microextraction (named MC-SPME) is a powerful technique proven to enhance the level of information on the volatile profile [1,2]. Shorter cumulative extraction times, using a low volume of sample to avoid headspace saturation proved effective for discriminating between different qualities of olive oil (i.e. extra-virgin, virgin and lampante oil) as well as the different geographical origins among the extra virgin oils. The use of a novel data mining and chemometrics software enabled automatic alignment of chromatograms and extraction of useful information in a simple and straightforward way, supporting the routine application of this approach to corroborate sensory panel analysis.

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VOLATILE MASS SPECTRAL FINGERPRINTING BY SPME MS FOR CLASSIFICATION OF HONEY BOTANICAL SOURCE

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Honey is greatly appreciated by consumers, not only for its nutritive properties and sweet taste, but also for its pleasant aroma which plays a significant role in honey selection by consumer. A number of honeys from different botanical source (unifloral, multifloral and honeydew honeys), holding distinctive organoleptic properties and with different commercial value, are marketed nowadays [1]. As frauds regarding mislabeling of honey botanical source are one of the most common [2], their identification is a subject of great interest not only for consumers but also for regulatory bodies.

In this study, volatile fingerprints by Headspace-Solid-Phase Microextraction followed by Mass Spectrometry (HS-SPME MS) have been evaluated as an alternative approach to the corresponding gas chromatography method (HS-SPME GC-MS) for classification of honey botanical source. The performance of four data sets, considering the use of carboxen/polydimethylsiloxane (C/PDMS) and polyacrylate (PA) SPME fiber coatings per approach, has been compared using different chemometric procedures. Irrespective of the approach, C/PDMS fiber provided better discrimination than PA. Stepwise linear discriminant analysis (S-LDA) of HS-SPME GC-MS data showed a very good classification capability (average classification error $< 1.8\%$), whereas optimal results were provided when HS-SPME MS data were subjected to PLS-LDA (average classification error $< 1.1\%$). Although citrus source was the most accurately classified by any of these two approaches, classification errors $< 3\%$ were obtained from MS fingerprints for all the five honey types here considered when the C/PDMS fiber was used. Therefore, HS-SPME MS is shown as an advantageous approach for the fast and accurate classification of samples in studies on honey source authentication.

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MOLECULARLY IMPRINTED POLYMER-HOLLOW FIBER MICROEXTRACTION OF HYDROPHILIC FLUOROQUINOLONE ANTIBIOTICS IN ENVIRONMENTAL WATERS AND URINE SAMPLES

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In the present work, the preparation of a new selective molecularly imprinted polymer (MIP) for the family of fluoroquinolones (FQs) in the pores of polypropylene hollow fibers (HFs) is proposed. The resulting MIP-HFs were used to develop a selective microextraction methodology (MIP-HFM) to determine selected FQs danofloxacin, norfloxacin, enrofloxacin and ciprofloxacin in real samples of environmental and biological interest. Measurements during the optimization of the MIP-HFM and its application to the analyses of real samples were performed by HPLC-UV and HPLC-MS/MS. In order to establish optimum rebinding conditions, the effect of key experimental parameters such as loading media, extraction time and stirring-rate were studied. The developed MIP composites exhibited recognition properties towards the selected hydrophilic antibiotics in non-polar media (toluene) and in polar protic systems such as methanol and methanol/water solutions, up to 20% water content. Recoveries by the developed method for all FQs tested in surface water, groundwater and urine spiked with the analytes of interest at two different concentration levels were within 9.4–24.5 %, with a relative standard deviation, generally <20% (n = 3). The detection limits were within 0.1–10 µg L^{-1}, depending upon the antibiotic and the type of sample.

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EVALUATION OF 2-HYDROXYETHYL METHACRYLATE AS CO-MONOMER IN THE PREPARATION OF WATER-COMPATIBLE MOLECULARLY IMPRINTED POLYMERS FOR THE EXTRACTION OF TRIAZINIC HERBICIDES

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In this work, a preliminary study on the use of 2-hydroxyethyl methacrylate (HEMA) as co-monomer together with methacrylic acid (MAA) in the preparation of water-compatible molecularly imprinted polymers (MIPs) for triazinic herbicides is presented. Four sets of MIPs and NIPs, with MAA:HEMA molar ratios in the polymerization mixture varying from 4:0 to 1:3 were synthesized using propazine as template molecule, and further evaluated for the direct recognition of several triazines of different polarity in aqueous media. Evaluation was performed by Molecularly Imprinted Solid-Phase Extraction (MISPE) on cartridges containing 100 mg of the different polymers obtained, loading 1 mL of an aqueous solution containing 500 ng of each selected triazine (separated experiments) which, after performing a washing step with 500 µL of acetonitrile, where eluted with 500 µL of methanol followed by 2 x 500 µL of a solution of methanol containing 10% of acetic acid. Elution fractions were evaporated to dryness and redissolved in 500 µL of Milli-Q water for final determination by HPLC-DAD at 220 nm. The results shown an important improvement on molecular recognition of triazines in water when HEMA was incorporated as co-monomer, both in 3:1 or 2:2 MAA:HEMA molar ratios, being the former selected as optimum since it provided the highest recoveries (up to 80% for PPZ). Breakthrough volume and capacity studies were also performed, and results are also presented herein.

DETERMINATION OF ZINC OXIDE NANOPARTICLES IN MOSTURIZING CREAMS BY SP-ICP-MS

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The use of zinc oxide nanoparticles (ZnONPs) in the cosmetic industry is in continuous growing due to their properties as ultraviolet filters. Inorganic filters do not generate allergic skin reactions and they are photostable unlike several organic filters. ZnONPs provide also antimicrobial properties so they can be used as preservative and ultraviolet filters at the same time, diminishing thus the production costs. The addition of nanoparticles to cosmetic products has to be noticed to the European Commission before their introduction into the market. Furthermore, the presence of nanoparticles in the list of ingredients by using of the word “nano” in brackets has to be clearly indicated in the cosmetic product [1].

In this communication, two different sample pre-treatments have been used to isolate ZnONPs from moisturizing creams before sp-ICP-MS analysis. One of the sample pre-treatments was based on ultrasonicating the moisturizers using acetone as an extractant solvent. Parameters of the ultrasonication procedure such as amplitude, time, solvent volume, and mode of ultrasonication can affect the extraction efficiency. Thus, this extraction procedure was optimized and the optimal parameters were 5 min, 40% of amplitude, 40 mL of acetone, and discontinuous mode (59 s of relax after 59 s ultrasonication). The other sample pre-treatment has consisted of the dispersion of ZnONPs from moisturizing creams in water after a defating step with hexane [2].

The over-all methodologies (sample pre-treatment and sp-ICP-MS determination) were validated and applied to several moisturizing creams with sun protection factor (SPF).

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EXPLOITING 3D PRINTED DEVICES MODIFIED WITH CORE-SHELL MOLECULARLY IMPRINTED POLYMERS BASED ON METAL ORGANIC FRAMEWORKS AS ON-LINE EXTRACTION MICROCOLUMNS FOR AUTOMATIC DETERMINATION OF BISPHENOLS IN SEAWATER

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Bisphenols (BPs) are plasticizers that are commonly used for the preparation of plastics and epoxy resins. Many of them are known as endocrine-disrupting chemicals or can cause genotoxicity and carcinogenesis even at low amounts, as Bisphenol A (BPA) [1]. Moreover, the presence of BPs in the environment is increasing due to the industrial waste pollution, and the occurrence of microplastics in aquatic settings that might release BPs in seawaters. In any case, the BPs in seawater are found at trace level concentrations and prior to their determination, sample preparation steps are thus needed. In this sense, the launching of 3D printing technologies in combination with automatic systems such as sequential injection analysis enables automation of unrivalled sample preparation approaches. However, the selectivity and absorption capacity of the 3D printed systems is rather limited. Regarding to this, its combination with molecularly imprinted polymers (MIPs) as low-cost selective smart materials for sample preparation is an interesting alternative to overcome the lack of selectivity of the 3D printed materials. Nevertheless, the early analyte breakthrough of MIPs jeopardizes the actual applicability in automatic on-line extraction procedures. To solve this problem, it is interesting to incorporate metal organic frameworks as a core for MIPs to ameliorate the breakthrough volumes and enhance extraction capabilities [2]. In this work, a 3D printed device containing a porous organic monolith was covalently modified with a core-shell MIP of BPA to extract BPs from seawater prior to their determination by HPLC-UV.

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LOW COST 3D PRINTED SPECTROPHOTOMETER FOR SUNSET YELLOW AND TARTRAZINE SIMULTANEOUS DETERMINATION

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The food industry is an important economic source in most countries of the world. The appearance of food is crucial in making it an attractive product. Thus, manufacturers often use different dyes, some of which are regulated in their use (with maximum allowed levels), while others are prohibited due to their hazardous consequences. Tartrazine (E-102) and sunset yellow (E-110) have been two of the most widely used dyes in recent years. Several of their adverse effects on human health are known [1]. The spectrometric behaviour of tartrazine and sunset yellow does not allow their direct quantification when both dyes are in the sample. Portable devices are valuable instruments for industrial quality control, and also for regulatory checks by competent authorities. Smartphone-based devices have been gaining more importance recently. The use of 3D printing technology has facilitated the manufacture of analytical interfaces adapted to perform image-based determinations with Smartphones. In this work, the study of real samples of powdered juices and gelatins was carried out with a 3D printed spectrophotometer (Figure 1). In all samples, tartrazine and sunset yellow were successfully quantified using imaging with the aid of Multivariate curve resolution-alternating least squares (MCR-ALS) as a chemometric tool. The recoveries ranged between 91 and 108.6%.

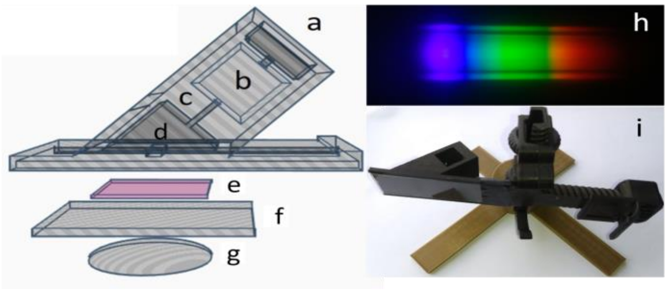

Figure 1. Detail of the spectrophotometer. a) Light entrance window b) Cuvette holder c) Slit d) Diffraction grating e) Glass slide f) Focus lens g) Visible spectrum capture h) Actual spectral image acquisition i) Real image of the device.

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DEVELOPMENT OF METHODOLOGIES TO OBTAIN BIOACTIVE PEPTIDES FROM POMEGRANATE SEEDS USING HIGH INTENSITY FOCUSED ULTRASOUNDS AND PRESSURIZED LIQUIDS

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The valorization of food by-products by the extraction of bioactive compounds has raised as an answer to reduce waste generation and to satisfy the demand for new and cheap functional ingredients. Processing of pomegranate generates by-products such as seeds, with high content in proteins and lipids. The lipidic fraction of the seed is exploited by the cosmetic industry, but no effort has been targeted to the reuse of the protein fraction (20% of the seed). The aim of this work was to develop analytical methodologies, based on high intensity focused ultrasounds (HIFU) and pressurized liquids (PL), for the exploitation of this residue to obtain bioactive peptides. The composition of the extracting buffer (pH and ionic strength), the addition of additives such as sodium dodecyl sulfate (SDS), the amplitude of the ultrasonic probe, and the extraction time were optimized for the extraction of proteins using HIFU while the temperature, the number of cycles, the composition of the extracting solvent (% EtOH and pH), and the static time were studied in the case of PL. Peptides were obtain from extracted proteins by *in vitro* gastrointestinal digestion, and antihypertensive, antioxidant and hypocholesterolemic properties were evaluated both in the protein extracts and in the hydrolysates. HPLC-ESI-QTOF-MS/MS, using two different chromatographic modes, enabled the identification of hydrophobic and hydrophilic peptides. Results shown that peptides released using different methodologies showed different characteristics and identities, which demonstrated the complementarity of both HIFU and PL; peptides obtained by HIFU highlighted for its antihypertensive activity, while the hydrolysis of proteins extracted by PLE boosted the protection against oxidative damage. Moreover, contribution to the bioactivity of other molecules different from peptides and proteins was also observed.

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SUITABILITY OF NATURAL DEEP EUTECTIC SOLVENTS IN COMBINATION WITH HIGH INTENSITY FOCUSED ULTRASOUNDS FOR THE SUSTAINABLE EXTRACTION OF PROTEINS

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Protein extraction usually requires the use of harsh and polluting organic solvents, which make necessary the development of alternative methodologies avoiding their use. Natural deep eutectic solvents (NADES) are considered green solvents due to their biodegradability and low toxicity. They are prepared from two natural, solid compounds mixed under certain conditions and proportions to form a solvent with a melting point lower than that of each individual component[1]. NADES have demonstrated to be useful for the extraction of small molecules such as polyphenols, but there is not much on its performance extracting big molecules as proteins. The aim of this work was to evaluate the potential of nine different NADES in the extraction of proteins from pomegranate seeds. Best extraction yield was observed with a DES constituted by choline chloride and acetic acid (ChCl:HAC). Extraction was carried out using high intensity focused ultrasounds (HIFU) to improve the extraction yield and to accelerate the process. An experimental design based on a Response Surface methodology was employed for the optimization of extraction parameters: temperature, ultrasound amplitude, time, and amount of sample. It was possible to extract 13.3 ± 0.4 g protein/100g seeds under optimal conditions which were: 27.8 mg of sample, 80% ultrasounds amplitude, and extraction time and temperature of 15 min and 60°C, respectively. The protein-enriched extract was characterized by studying its potential to obtain peptides with antioxidant properties, after *in vitro* gastrointestinal digestion. Moreover, proteomics techniques and high-resolution mass spectrometry were applied for the identification of extracted proteins and peptides responsible for this bioactivity. Results were compared with those obtained using pressurized liquids and non-sustainable solvents.

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GREEN SOLVENTS FOR SUSTAINABLE RECOVERY OF HIGH ADDED-VALUE VANILLA COMPOUNDS FROM WASTEWATER

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Agri-food industries generate large amounts of waste, which is a sustainable and low-cost resource. Therefore, the recovery of high added-value compounds from by-products through eco-friendly extraction processes is currently of great interest.[1] The main compounds derived from vanilla (vanillin and vanillic acid) are known for their antioxidant and beneficial properties for human health with application in the pharmaceutical, food and cosmetic industries.[2,3] Due to the high cost of natural vanilla, the world's most popular flavoring, the recovery of valuable compounds from vanilla effluents is an attractive strategy to promote decontamination and revaluation of wastewater.[2,4] In this work, an efficient and environmentally friendly liquid-liquid extraction process was developed for the sustainable recovery of vanilla derived compounds from aqueous environments. Three hydrophobic bio-based solvents (2-methyltetrahydrofuran, cyclopentylmethyl ether, and *D*-limonene) and three hydrophobic eutectic solvents based on menthol and natural organic acids were evaluated as potential alternative extractants to conventional volatile organic solvents, such as ethyl acetate. Subsequently, the extracted compounds were quantified by UV-Visible spectrophotometric and chromatographic (HPLC-DAD) methods. Extraction efficiencies were studied in terms of stirring time, solvent:feed volume ratio and initial concentration. Overall, the results supported that 2-methyltetrahydrofuran provided the best recovery results of up to 95.37 ± 0.18 % for vanillin and 91.96 ± 0.38 % for vanillic acid with good repeatability (RSD <0.40 %) from the aqueous vanilla extracts. In addition, aiming at full sustainability, solvent recycling and reuse in consecutive extraction cycles was successfully achieved. This approach enhances the development of new strategies for revaluation and/or cleaning of agricultural waste based on sustainable solvents.

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MESOSTRUCTURED SILICA FUNCTIONALIZED WITH ACID SULFONIC GROUPS AS SORBENT FOR DISPERSIVE SOLID PHASE EXTRACTION OF TROPANE ALKALOIDS FROM AROMATIC HERBS AND SPICES

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Tropane alkaloids (TAs) are a family of natural toxins made up of more than 200 compounds [1]. The most representative compounds of this family are atropine and scopolamine that are produced by plants of the *Brassicaceae, Solanaceae* and *Erythroxylaceae* families, among others. The intake of these toxins can produce negative health consequences, as they are antimuscarinic compounds. The occurrence of TAs in cereals, legumes, teas and herbal teas, aromatic herbs, spices, etc. is due to the accidental harvest of these foods together with TAs-producing plants. Sample preparation is an important step in the extraction of these compounds. In this regard, to reduce matrix interferences, a new analytical methodology using silica-based materials was developed in this study. A SBA-15 silica was synthesized and functionalized with sulfonic acid groups (SBA-15-SO_3^-) according to a previous work [2]. Likewise, an HMS type silica was prepared and functionalized with the same ligand as the SBA-15, following the same protocol (HMS-SO_3^-). Both materials were used as strong cation-exchange sorbents in dispersive micro solid phase extraction (d-µ-SPE) of atropine and scopolamine from aromatic herbs and spices. The method involved a solid-liquid extraction with an aqueous-acid medium (pH 1, HCl), followed by purification of the extract by d-µ-SPE. The sample extracts obtained were analyzed by high performance liquid chromatography coupled to a triple quadrupole mass spectrometry detector with an ESI in positive ion mode. The materials tested showed good recoveries above 70 % for both analytes. The method developed was successfully applied to determine atropine and scopolamine in different commercial samples.

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MULTI-RESIDUE DETERMINTION OF ACRYLAMIDE AND FURANIC ALDEHYDES IN INSECT-BASED FOODS USING FUNCTIONALIZED MESOSTRUCTURED SILICA FOR SAMPLE PREPARATION PRIOR LC-TQ-MS/MS ANALYSIS

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Insect-based foods can contribute to our diet by providing high-quality proteins, healthy fats, and micronutrients, such as calcium or iron. Despite their good nutritional characteristics, their safety has been scarcely studied. Thus, it is necessary to collect data on some organic compounds, such as process contaminants like acrylamide (AA) and furanic aldehydes (e.g. hydroxymethylfurfural (HMF), 5-methylfurfural (MF) or furfural (F)) [1]. These compounds are being controlled in a variety of foods due to their genotoxic and carcinogenic effects. Their formation depends on the ingredients and the food processing conditions [1]. At present, many insects-based foods are made with a high content of sugar and proteins that can induce the formation of these harmful compounds. In our previous work, high concentrations of HMF were quantified in cereal and insect bars [2]. Accordingly, in this study, the levels of AA, HMF, MF and F are evaluated in different commercial samples made with insects (bars, crackers, flours), particularly with cricket (*Acheta domesticus*). For this purpose, a large pore mesostructured silica of the SBA-15 type was synthetized and functionalized with aminopropyl-groups (SBA-15-LP-NH_2). The material was applied as sorbent in solid phase extraction (SPE) of AA, HMF, MF and F. The optimized method involved a solid-liquid extraction with 10 mL of acidified water (pH 1, HCl) and 0.1 mL of Carrez I and II, followed by the purification of the sample extract (1 ml) by SPE using 100 mg of material. The simultaneous analysis of the four target compounds was carried out by liquid chromatography coupled to triple quadrupole mass spectrometry (LC-TQ-MS/MS). Depending on the food matrix, recoveries varied between 53-79 % for AA, 78-101% for F, 56-115% for MF and 57-105% for HMF. The method was successfully applied, detecting HMF and MF in different insects-based foods samples.

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MESOPOROUS SILICA-COATED MAGNETIC NANOPARTICLES TO EXTRACT SIX OPIUM ALKALOIDS IN EDIBLE POPPY SEEDS PRIOR TO HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY ANALYSIS

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In recent years, health authorities have become increasingly concerned about preventing consumer exposure to opium alkaloids in poppy seeds. Therefore, there is a need to develop new effective methods to determine them [1]. Until now, studies have mainly considered only morphine, but EFSA has recommended to include all main alkaloids present in poppy seeds (morphine, codeine, thebaine, papaverine, noscapine and oripavine) [2]. In this study, a simple, rapid and efficient method has been optimized to determine these six main opium alkaloids in poppy seeds by high-performance liquid chromatography coupled to a triple quadrupole tandem mass spectrometry detector. Firstly, solvent extraction (SLE) was optimized: seeds amount (2.5 g), solvent (50% methanol/water), volume (30 mL), time (30 min), consecutive extractions number (2) and pH (6.8). Then, six different adsorbent magnetic materials were evaluated for magnetic solid-phase extraction (MSPE). Materials were formed from a core of Fe_3O_4 coated with non-porous (Fe_3O_4@nSiO_2) and mesoporous silica (Fe_3O_4@nSiO_2@mSiO_2) both functionalized with octadecyl-silane (C_{18}) or octyl-silane (C_8). Then, particles were characterized and adsorption studies at different times (1-20 min) were carried out to compare them and select the most effective one. Finally, materials with mesoporous silica showed higher adsorption percentages and the best was Fe_3O_4@nSiO_2@mSiO_2 due to its higher surface area (332.79 m^2/g) and higher adsorption capacity of all analytes (between 60 and 80% in 1 min). The parameters of the MSPE procedure were optimized: adsorption time (1 min), material amount (100 mg), desorption solvent (diethyl ether/methanol, 80/20, v/v with 10% ammonia), desorption time (1 min), desorption solvent volume (2 mL) and desorption number (2). Recoveries after purification were of 79-105% for all analytes except for morphine and oripavine which was near to 50%. The optimized method was used to analyze the presence of these six opioids in different edible poppy seeds from national supermarkets and all of them showed contents of all alkaloids.

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IDENTIFICATION OF VOLATILE COMPOUNDS IN EPOXY AND ORGANOSOL COATING BY P&T GC-MS

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The internal surface of metal cans for food packaging is frequently covered with a coating. Epoxy and organosol are some of the resins widely used. Components from the coating may migrate into the foodstuffs. Therefore, the coatings should be evaluated for their safety for food contact. The aim of the present study was to investigate volatile compounds from epoxy and organosol coating by using Purge and Trap (P&T) system coupled to GC-MS. This technique provides headspace samples by purging with He as inert gas. The chromatographic analysis was performed under the following conditions: capillary column Rxi-624SilMS (30 m x 0.25 mm, 1.4 µm), oven ramp temperature was from 40 to 250 °C, transfer line 300 °C, detector temperatures 200 °C, carrier gas He, and flow rate of 1 ml/min. The mass range captured was between 20-500 m/z. Spectral libraries specifically, NIST MS (version 2.0) and Wiley RegistryTM 8th edition were used for identification purposes. The most abundant substances identified were compounds with benzene structure, aldehydes such as pentanal, hexanal, nonanal or decanal and alcohols such as 1-butanol were also identified and confirmed with a standard solution. Furthermore, a method to quantify some of the identified compounds was explored. The analytes were quantified by using calibration plots prepared spiking a solid matrix with a standard solution. Appropriate determination coefficients (r^2> 0.99) were obtained.

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MIGRATION OF COMPONENTS FROM EPOXY CAN COATINGS AND ANALYSIS BY LIQUID CHROMATOGRAPHY

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Epoxy resins are used as internal surface coating for food and beverage cans. The success of these epoxy formulations as coatings is due to its desirable flavour-retaining characteristics, its excellent chemical resistance and its outstanding mechanical properties.

Epoxy resins are obtained by the condensation of epichlorohydrin and bisphenol A (BPA), which yields bisphenol A diglycidyl ethers (BADGEs). If the reaction process or curing conditions are not applied in a proper way, and therefore the finished coating is not correctly crosslinked, these components together with potential unreacted substances/oligomers could migrate and reach the food. European Legislation establishes migration levels for BADGE, and its hydrolysis (BADGE.H_2O and BADGE.$2H_2O$) and chlorohydroxy (BADGE.HCl, BADGE.2HCl and BADGE.H_2O.HCl) derivatives; however, is lacking for other compounds.

The objective of this work was to perform a migration study for the identification of these potential unreacted substances. Firstly, the polymeric coating was identified using an ATR-FTIR spectrometer equipped with a diamond optical crystal and by confocal Raman microscopy. The can used in this study, intended for beverages, was provided by an industrial partner. One side migration tests were carried out using ethanol 95% as food simulant for 10 days at 40 ºC (in duplicate) using migration cells. Then, the separation and identification of compounds was performed by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) in full scan mode detection.

Several non-intentionally added substances (NIAS), specifically oligomers of BADGE were identified in the migration extracts analysed including cyclo-di-BADGE, among others.

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SPME-GC-MS ANALYSIS OF POTENTIAL VOLATILE MIGRANTS FROM EPOXY AND ORGANOSOL COATINGS USED IN METAL FOOD CANS

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Polymeric coating can be applied to the food contact surface of metal cans to preserve food and protect metal from corrosion. Components from the coating may potentially migrate into the food and represent a risk for the consumers' health. The identification of potential migrants is essential to evaluate the chemical safety of the coatings. The aim of this work was to identify volatile compounds from epoxy and organosol coating by using a GC-MS technique. Volatile compounds were analysed by using Solid Phase Microextraction (SPME) coupled to GC-MS. A SPME holder for manual sampling and a Divinylbenzene-carboxen-polydimethylsiloxane (DVB/PDMS/CAR) fibre with 50–30 µm thickness fibre was used in the study. The chromatographic separation was performed on a Rxi-624SilMS (30 m x 0.25 mm internal diameter, 1.4 µm thickness) column. The oven ramp temperature was from 45 to 250 °C, and the transfer line and detector temperatures were set at 250 and 200 °C, respectively. Data analysis was performed using Xcalibur version 2.0.7. NIST/EPA/NIH 11 mass spectral library (version 2.0) and Wiley Registry TM 8th edition database were used for the identification of the compounds. SPME-GC-MS has shown to be a useful tool for the analysis of volatile migrants from the polymeric coatings used in food contact materials. Some aldehydes such as octanal, nonanal or decanal were identified in the samples analysed. Other compounds such as dimethyl pentanedioate or diethyl phthalate, which is a plasticizer widely used in resins and polymers were also identified.

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NON-TARGETED ANALYSIS FOR THE IDENTIFICATION OF VOLATILE COMPOUNDS FROM A POLYESTER COATINGS BY GAS CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY

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Polymeric coatings are complex formulations commonly applied on the internal surface of food and beverage metal cans to act as a barrier between the product and the metal, being crucial to preserve food quality. As a consequence of the toxic effects reported in epoxy resins, polyester coatings are currently used as a first-generation alternative. Polyester-based coatings are produced from polycondensation reactions between carboxylic acids and poly-functional alcohols in excess. However, its components could migrate into the foodstuffs and represent a risk to the health of consumers, therefore they should be evaluated.

The aim of the present work was to identify volatile compounds from a polyester coating using gas chromatography coupled to mass spectrometry (GC-MS) with a purge and trap (P&T) technique. Different parameters, such as temperature, time, and sample amount were optimized, and the chromatographic separation was performed on a Rxi-624Sil MS (30 m × 0.25 mm internal diameter, 1.40 µm film thickness) column. Helium was used as carrier gas at a constant flow rate of 1 mL/min; the oven program was initially set at 45 ºC for 4 min, then increased at a rate of 8 ºC/min until 250 ºC and held for 5 min; the transfer line and source temperature were set at 250 ºC and 200 ºC, respectively. Compounds were identify using the commercial mass spectral libraries NIST/EPA/NIH 11 (version 2.0) and Wiley Registry^{TM} 8th edition

It was observed that at higher purge temperatures a greater number of compounds were detected. Several aldehydes, alcohols and aromatic compounds (composed of at least a benzene ring into their structures) were detected. Some of them could be confirmed by injection of the respective standard.

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AMINO-FUNCTIONALIZED SILICA FROM RICE STRAW: NITRATE ADSORPTION

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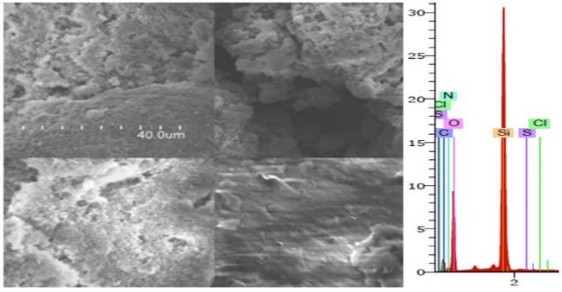
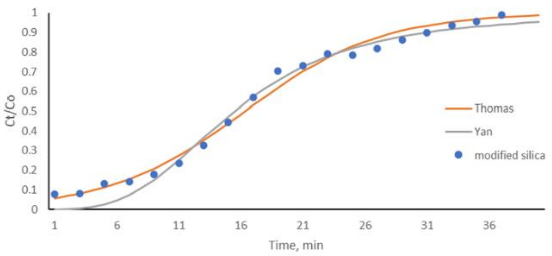
In Europe, the 87% of groundwater contains excess of nitrates (Europe's Water: An Indicator-Based Assessment), which causes: eutrophization, soil acidification, air pollution and at high levels produces carcinogenic nitrosamine in drinking water [1]. Current available technologies such as reverse osmosis or biological denitrification are used for water treatment, but these methods are expensive and generate additional by-products enriched with nitrate, between others. Adsorption systems can be an option more economical and eco-friendly. Here, we propose to use an agricultural waste, the rice straw, to produce a green adsorbent bed capable to remove nitrate from water. The beds were obtained by extraction and amino-modification of silica obtained from rice straw [2]. This work is included in the LIFE-LIBERNITRATE project, which pretend to use the beds to eliminated 30% of nitrate of the comprehensive water cycle in several planned scenarios [1]. The adsorption process has been studied at lab scale in both, static and dynamic mode, by breakthrough curves, showing better result for continuous flow system. It was found that Yan mathematical model fits better to the experimental data than the Thomas one, which is indicative to the formation of a monolayer coverage of the adsorbent surface. Adsorption capacity of nitrate has been investigated at different bed high, flow rates, standard nitrate concentrations and real samples from a developed device, which permits to scale-up the results. The maximum adsorption capacity for standard nitrate was found 68.5 mg of nitrate per g of adsorbent.





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STUDY OF FILTER BASED EXTRACTION OF CARBON BLACK NANOPARTICLES BY USING AF4-DLS

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Carbon Black (CB), is a carbon based material that involves an important challenge for Analytical Chemistry. The interest of CB relies on environmental, industrial and biological analysis since this material can be found in these matrices due to its use in different processes. Thus, its extraction, determination and/or elimination due to its potential toxicity is required [1]. The objective of the present work was the evaluation of filter-based extraction of CB nanoparticles dispersed in different dispersants (cellular culture medium and polymeric) using membranes with different nature (fiberglass, nylon filter and teflon) and pore size (0.1 to 2 µm). Asymmetrical flow field flow fractionation coupled to DLS (AF4-DLS) has been used to monitor the extraction efficiency.

DLS-fractograms showed that pore size, filter and dispersant nature had a significant role in the extraction efficiency. Polymeric dispersions resulted in quantitative extractions, however, for cell culture medium extraction up to 10 % were achieved using membranes with pore size > 0.45 µm. These results can be explained considering the particle size of CB nanomaterial (386 nm for polymeric and 175 nm for cellular) and zeta-potential which was 22.6 mV and -18.6 mV for polymeric and cell dispersant, respectively. AF4-DLS was demonstrated to be a potential analytical tool for CB analysis showing adequate sensitivity and precision (LOD of 0.4 mgL^{-1} and RSD < 10%).

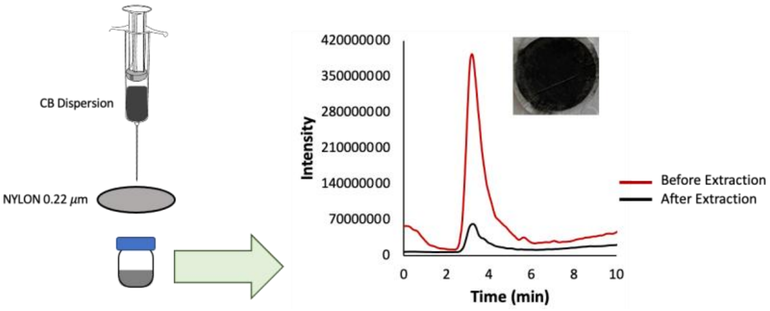

Figure 1: CB extraction system and DLS-fractograms obtained for polymeric dispersant

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NANO-LIQUID CHROMATOGRAPHY: FROM LAB TO PORTABLE EQUIPMENTS

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Miniaturized LC systems have emerged as a consequence of the reduction of the column internal diameter, which comes along with a reduction in mobile phase flow rates. The use of miniaturized systems offers several advantages over conventional LC, such as reduction of sample dilution, lower waste treatment costs, use of lower sample amounts and sustainability [1]. This work aims to evaluate the capabilities of two Nano-LC systems for the determination of different groups of target analytes: a benchstop Nano-LC coupled on-line to in-tube solid phase microextraction (IT-SPME) and a portable Nano-LC. Analytical parameters such as sensivity, LODs, and resolution have been studied. Futhermore, for the portable Nano-LC robustness and stability in the field have been tested. This study has allowed to conclude that lab IT-SPME-Nano-LC provides higher sensitivity as spected. On the other hand, chromatograms obtained with portable Nano-LC have much higher resolution allowing to detect more peaks in a shorter analysis time. With respect to in field performance, portable Nano-LC increased baseline noise working at high humidity and low temperatures, but the chromatographic profile was conserved.

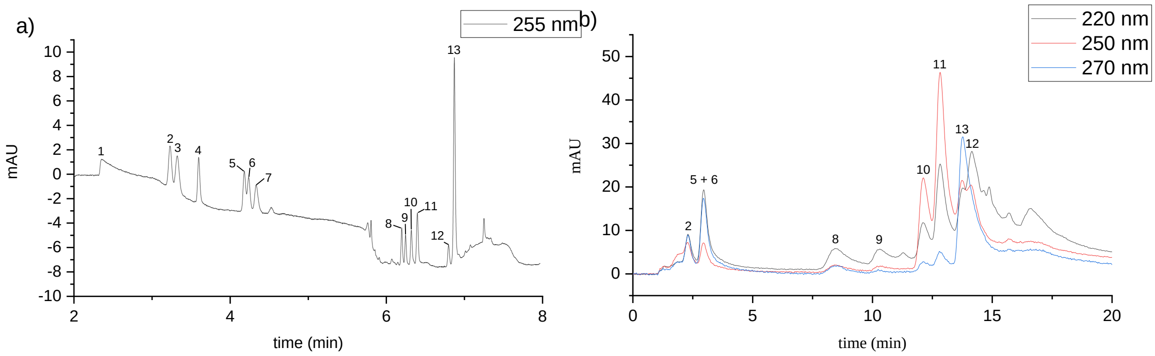

Fig. 1. Chromatograms obtained for a multicomponent mixture of different groups of target analytes with a) a portable Nano-LC and b) a lab IT-SPME-Nano-LC. Concentrations of each analyte are 10 - 60 mg L^{-1} (a) and 20-120 µg L^{-1} (b).

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TESTING SAMPLE INTEGRITY AFTER DILUTION BY USING SEVERAL MINIATURIZED LIQUID CHROMATOGRAPHY TECHNIQUES

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Error made due to dilution of the sample and its impact on the final results is many times not paid attention to when conducting system comparison studies. Nowadays, conventional chromatographic methods are moving towards miniaturization due to their multiple advantages [1]. Miniaturized methods are in full development, and the question arises as to whether a mistake can be made in the quantification of samples. Conventional chromatography offers the possibility to inject more concentrated samples, which may lead to matrix effects as it is poorly or none diluted. To inject samples with analyte content at ppm levels in micro or nanoLC, important dilutions are needed sometimes, which eliminates the matrix effects but may imply errors due to the dilution itself [2]. To study these phenomena, a comparison among three different chromatographs, microLC, nanoLC and portable nanoLC, has been made. The sample was injected directly into the portable nanoLC and diluted 5000 and 10000 times for injecting in the lab capLC and nanoLC, respectively. For the analysis in cap and nanoLC the sample was cleaned-up using IT-SPME. LOD's, BIAS, RSD and recovery were evaluated for all three chromatographs for the lower and upper levels of concentration tested.

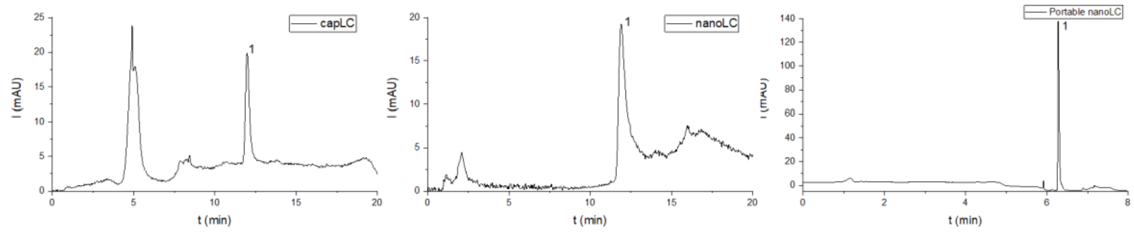

Figure 2. Obtained chromatograms for a sample of water containing pyrimethanil (1). From left to right, chromatograms obtained with IT-SPME capLC, IT-SPME nanoLC and portable nano LC.

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CHARACTERIZATION OF DIETARY SUPPLEMENTS BY PORTABLE HIGH PERFORMANCE NANO-LIQUID CHROMATOGRAPHY

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The consumption of supplements in the diet has grown increasingly over the past years with different purposes, thus making necessary to analyze their main ingredients to verify if they are within the limits of safety for human consumption and to avoid fraud[1]. In this work we describe a method for the determination of seven compounds usually present in a variety of supplements of botanical origin with potential benefits for health, namely caffeine, riboflavin, theobromine and several chlorogenic acids: 5-chlorogenic acid (5-CQA), Isochlorogenic acid A, Isochlorogenic acid B and Isochlorogenic acid C. These compounds have been separated by portable high performance nano-liquid chromatography and detected at 255 nm; the target compounds were previously extracted from the samples using an ultrasound assisted extraction protocol. The proposed conditions allowed the quantification of the analytes at the point of need with limits of detection for the different compounds between 1 and 30 mg L^{-1}. The method has been applied to the characterization of different dietary supplements, mainly containing extracts of green coffee.

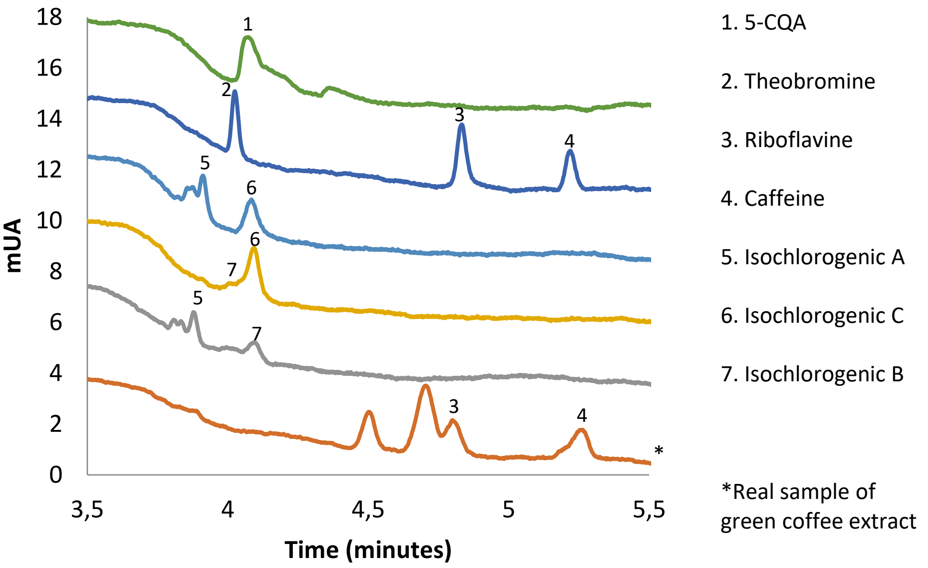

Figure 1. Chromatograms of several standards and a dietary sample

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APPLICATION OF ENZYMATIC ASSAYS FOR THE DETECTION OF CHEMICAL CONTAMINANTS IN FOOD: THE IMPORTANCE OF EXTRACTION AND SAMPLE TREATMENT

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Last trends have shown that fast and simple detection methods are gaining importance in food quality and safety control as screening methods. On this matter, the developments of biosensors, and specifically of enzymatic biosensors, are increasing due to their specificity and selectivity [1,2]. As chromatographic techniques, biosensor analysis also requires an efficient removal of interferences, which is vital to reduce the matrix effect during the detection steps [3].

In the present work, distinct extraction and sample treatment protocols, compatible with enzymatic assays, were evaluated for the detection of diverse chemical contaminants in different food matrices. The control of legally regulated contaminants and the assessment of the presence of emerging contaminants in food is crucial, thus, polycyclic aromatic hydrocarbons (PAHs), perfluoroalkylated substances (PFAS) and pesticides were selected as target analytes in this work.

First, the extraction was made using organic solvents and modified QuEChERS procedures. Next, further clean-up was needed for the removal of interferences causing high matrix effect in the enzymatic assays. For this, solid phase extraction (SPE) cartridges were selected considering the nature of target analytes and interferences from each food matrix. After optimization of extraction protocols the improvement of the matrix effect on the detection of target contaminants by enzymatic assays was evaluated. A compromise was reached between an adequate clean-up of the food sample extract and the recovery values of contaminants, always considering that the final extract medium must be compatible with the enzymes. As a result, protocols to extract and detect PAHs and PFAS in fish and pesticides in plant-based foods were developed.

Acknowledgement

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ENZYMATIC EXTRACTION FOR THE ANALYSIS OF SILVER NANOPARTICLES IN CULTIVATED MUSSELS

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In recent years, the use of silver nanoparticles (Ag NPs) has increased exponentially in the industry due to their strong antimicrobial and antibacterial properties. Their application in the textile industry, cosmetics, and water disinfection, among others, can result in emissions into wastewaters and affecting the environment. The common wastewater treatment plants do not have appropriate techniques to remove nanomaterials. Then, silver nanoparticles can react and release ions, being toxic for aquatic organisms. In Spain, one of the most cultivated aquaculture species is the mussel (*Mytilus galloprovincialis*). They are filter-feeding bivalve molluscs, and they can bioaccumulate nanoparticles and other different toxic compounds. Thus, ensuring food quality is needed to protect customers.

Nowadays, nanoparticle extraction from organisms remains a challenge and simple, cheap, and eco-friendly methodologies are required. An enzymatic extraction procedure was carried out in this study to ensure the integrity of nanoparticles. This extraction uses a pancreatin: lipase mixture (0.3 g L^{-1}/0.3 g L^{-1}) prepared in a buffer of NaOH: NaH_2PO_4 (0.2 M/0.2 M) at physiological pH (7.4). The fresh minced mussel meat was mixed with the enzymatic solution and incubated in a Boxcult incubation chamber for 12h under continuous stirring (orbital-horizontal shaking at 150 rpm and 37 °C). Afterwards, the extracts were filtered (5µm filter), diluted with 1% of glycerol and analyzed by single-particle ICP-MS (SP-ICP-MS). Finally, the developed methodology was applied to different cultivated mussel samples from the Atlantic area.

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OVERCOMING LIMITATIONS OF TRADITIONAL SPME FIBERS THROUGH NOVEL FABRICATION TO DETECT PAHS IN WATER AND BABY FORMULA IN THE PARTS-PER-TRILLION REGIME

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous chemical compounds produced by the incomplete combustion/incineration of organic materials, including municipal waste, wood, coal, cigarettes, and other fossil fuels. Typical analysis of PAHs uses gas chromatography and high-performance liquid chromatography as recommended by the US EPA. However, samples that must be monitored for PAHs often consist of matrices that complicate analyses and require extraction. Accordingly, the resulting isolation processes are traditionally done as multistep, complex procedures such as liquid-liquid phase extraction or solid phase extraction. The use of solid phase micro-extraction (SPME) is a single step process that includes extraction, isolation, and preconcentration. Further advances of SPME has its own set of advantages and disadvantages, which, depending on the fiber, include high or low extraction efficiency, small or large amounts of carry over, and good or poor bleed instability. Using physical vapor deposition (PVD) and chemical vapor deposition (CVD) of silanes, we have developed a novel fabrication method for fibers that overcome some of these limitations. Here, we compare a set of fibers created with this fabrication method to traditional, commercially available PDMS fibers. A fiber created with 2.8 µm thick sputtered silicon layer had comparable performance with a commercial 7 µm PDMS fiber for lower molecular weight (MW) PAHs in water. This fiber has ca. 3 times extraction efficiency for higher MW PAHs, with better linearity (0.5-125 ppb), repeatability (5-24%), and detection limits (7-64 ppt). PAHs in baby formula were also investigated. Our fiber showed good linearity (0.5-125ppb), repeatability (2-26%), detection limits (0.12-0.81 ppb), and recoveries (103-135%). The detection limit for our fiber for benzo[a]pyrene is similar to the commercial fiber, but our fiber shows less carry-over and phase bleed.

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EXTENDING THE APPLICABILITY OF FULLY AUTOMATED HIGH-CAPACITY SORPTIVE EXTRACTION FOR GAS CHROMATOGRAPHY MASS SPECTROMETRY

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High-capacity sorptive extraction techniques are increasingly being used to enhance the extraction of volatile organic compounds (VOCs) from a range of sample types, including foods, beverages and environmental water and soil. Commercially-available extraction phases have been limited to a rather narrow range of chemical sorbents, dominated in popularity by the 100% poly(dimethylsiloxane) (PDMS) sorbent phase, a polyacrylate (PA) phase and a hybrid offering with PDMS as copolymer to a more polar yet temperature-sensitive semi-solid of polyethylene glycol (PEG). This means that desorption temperatures are restricted for these polar phases, which can lead to inefficient release of analytes (that need higher temperatures) from the phase and into the analytical system. Although the technique provides a solvent-free approach with few sample preparation steps compared to conventional techniques, such as liquid-liquid extraction (LLE), the sample extraction process remains quite manual, with the analyst having to insert the extraction device (supporting the extraction phase) into the sample vial and, after extraction has finished, removing, washing and drying the device, before transfer to an instrument for analysis. Here, we present the evaluation of new phases intended to extend the applicability of high-capacity sorptive extractions for VOCs in a fully-automated workflow, from sample extraction, through to washing, drying and injection of analytes, and for synchronous analysis by gas chromatography-mass spectrometry (GC-MS). This means that as well as enhancing VOC extraction, there are few demands placed on the analyst, enabling high, unattended sample throughput, and faster reporting of results.

COMBINING HPTLC WITH FIBER OPTIC PROBE-MINI-SPECTROPHOTOMETER COUPLED TO SMARTPHONE FOR IN SITU ANALISIS: LACTOSE QUANTIFICATION IN SEVERAL MATRICES

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Over the last decades in the field of Analytical Chemistry there has been a grow interest on the development of analytical methods based on the principles of Green Analytical Chemistry, in order to have sustainable methodologies [1]. Besides that, society is demanding rapid in situ methods for real applications in food industries using new technologies. In this sense, milk is the most important European Union agricultural product in terms of value [2] representing 4% from the whole food industry [3]. Lactose is one of the major components in cow milk (40–50 g/L) and approximately 75% of the world's population has intolerance to this sugar. Because of the problems associated with lactose intolerance, the quantification of lactose is an important challenge in many areas of economic interest. Accordingly, in this work, a new sustainable analytical method have been proposed based on HPTLC for in situ detection and quantification of carbohydrates (e.g. Lactose) in real samples. Different carbohydrates have been separated and derivatized on HPTLC using a Thymol-Sulphuric acid ethanolic solution for plate development. The derivative products formed have been spectrophotometrically measured by using a fiber optic pro coupled to a mini-spectrophotometer-smartphone. As a case of study, the methodology has been applied to the determination of lactose in milk, lactose free-milk and hyssops collected from different critical points of a dairy food industry in order to control the presence or absence of traces of lactose. The achieved limits of detection were 0.03 mg L-1 or 0.003 mg L-1 in function of the required concentration ranges. Sample analysis were performed satisfactorily in terms of accuracy and precision obtaining RE values <8% and RSD values <2%.

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MIGRATION STUDY OF ANTIOXIDANT COMPOUNDS FROM ACTIVE FILMS DEVELOPED WITH EXTRACTS YIELDED FROM INDUSTRIAL FRUITS BYPRODUCTS

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Fruits by-products are significant sources of antioxidant compounds with potential application as food additives and to develop active packaging [1]. Antioxidant extracts yielded from tomato and lemon by-products produced by the food industry were incorporated into three different polymeric matrices: low-density polyethylene (LDPE), polylactic acid (PLA), and G-polymer to develop active films. The specific migration assays were performed to study the release of the active compounds to food simulants and evaluate their antioxidant properties, taking into account the final application as food packaging films. The identification and quantification of phenolic compounds that migrate to the food simulant were performed by high-performance liquid chromatography with a diode array detector (HPLC-DAD) [1]. The results showed that the films with lemon extract were those with the highest number of active compounds. Considering the different polymeric matrices, the PLA allowed a higher release of active compounds followed by G-polymer and finally LDPE. The eriocitrin and hesperidin were the main compounds released from the G-polymer and PLA films with the lemon extract. Considering the films containing tomato extract, the compounds that migrated in high amounts from the G-polymer were protocatechuic acid and rutin, while from the PLA films were caffeic acid, chlorogenic acid, and p-coumaric acid. The migration of active compounds from the LPDE films was low in comparison with the other polymeric matrices. PLA films with lemon extract were those that displayed high antioxidant capacity and the most promising to be used as active packaging to increase the shelf life of fatty foods.

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USE OF BIOMEMBRANES FOR THE SELECTIVE ELECTROMEMBRANE EXTRACTION OF FLUOROQUINOLONES FROM BIOLOGICAL SAMPLES

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Fluoroquinolones (FQs) are a group of synthetic heterocyclic drugs structurally derived from quinolone with antibacterial properties that have been widely used as antibiotics for treating different kinds of infections, especially digestive, pulmonary and urinary ones. In the last years, their consumption and dosage has increased, affecting negatively to the biota because of their presence as pollutants in urban wastewater, leading to the appearance of bacterial resistance to these antibiotics and, consequently, being recently included in the list of emerging pollutants [1-2]. Due to their high negative impact on the environment, analytical methodologies able to detect and quantify little amounts of these compounds in different types of samples (biological and/or environmental) are needed. In this work, a selective electromembrane extraction (EME) procedure of three selected FQs of veterinarian use is proposed. For this purpose, a chitosan biofilm (60% (w/w) chitosan, 40% (w/w) Aliquat®336) has been used as biopolymeric support, demonstrating an active role in the selective extraction of marbofloxacin (MRB), enrofloxacin (ENR) and flumequine (FLM) in the presence of other FQs, from animal urine samples. As derived from chitin, the polymeric chains of chitosan present free hydroxyl and amine groups which lead to possible interactions through hydrogen bonding. Amine groups with pKa values close to 6.5 favor the biopolymer to be positively charged in acidic or neutral media, allowing the use of this biomaterial for the selective extraction of polar active compounds. Within this realm, the interaction mechanism occurring between target FQs and the biopolymer has been deeply studied using Density Functional Theory calculations. This fact, together with its excellent biological and physiochemical properties (gelation ability, non-toxicity, antimicrobial activity, biocompatibility or biodegradability), make chitosan an excellent material for applications in the field of the Green Chemistry [3], as well as, an attractive alternative support for drug delivery compared to other materials traditionally used as supports in EME of pharmaceuticals.

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GREEN EXTRACTION APPROACH OF NON-EXTRACTABLE PHENOLIC COMPOUNDS FROM MANGOSTEEN PEEL BY ULTRASOUND ASSISTED EXTRACTION AND NATURAL DEEP EUTECTIC SOLVENTS

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Mangosteen (*Garcinia mangostana* L.) peel is a potential source of phenolic compounds, which can provide beneficial effects in terms of health promotion, and this byproduct is usually discarded. Generally, the studies have been focused on the extraction of polyphenols from plant matrices employing aqueous-organic solvents, without paying enough attention to bound polyphenols that remain retained in the extraction residue after conventional extraction with organic solvents, called non-extractable polyphenols (NEPs). A new generation of more sustainable solvents known as natural deep eutectic solvents (NaDES) has been considered to replace conventional organic solvents. NaDES are environmentally friendly, easily synthesized, biodegradable, non-volatile, highly stable, and have a low cost. NaDES present a great potential for extraction processes increasing extraction yields as well as protecting the degradation of bioactive compounds. The main aim of this work was to develop a green extraction methodology using ultrasound-assisted extraction (UAE) and NaDES for the extraction of antioxidant NEPs from mangosteen peel. To select the best NaDES to extract NEPs from mangosteen peel, seven NaDES were studied. Antioxidant capacity, and total phenolic and proanthocyanidin contents, as well as, molecular weight by chromatography size exclusion, were evaluated. The NaDES composed of choline chloride: lactic acid with a molar ratio of 1:2 was selected as the best solvent to extract antioxidant NEPs with low molecular weight from mangosteen peel. A Box-Behnken experimental design was employed to optimize UAE and other extraction conditions: water content (10-30%, v/v), ultrasound amplitude (30-60%), and extraction time (1-15 min). Ultrasound amplitude and extraction time have a positive effect on the extraction of antioxidant NEPs from mangosteen peel while the molar ratio of water presented a negative effect.

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A NOVEL COPPER NANOPARTICLE-BASED COLORIMETRIC METHOD FOR DETECTION OF GLYPHOSATE AT ROOM TEMPERATURE

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Glyphosate is currently a controversial chemical – it is one of the most widely used herbicides worldwide, but was also recently banned from some European countries due to its upgraded World Health Organization (WHO) classification as "probably carcinogenic to humans" (Group 2A). Standard analytical methods for glyphosate detection involve sample collection, transportation, preparation and analysis through high performance liquid chromatography/mass spectrometry (HPLC/MS). This is time consuming, expensive and non-portable. A novel fast and low-cost method for in-situ analysis of glyphosate is presented here. This new method is based on the peroxidase like activity of citrate-capped copper nanoparticles (CuNPs) in the reaction of 3,3′,5,5′-Tetramethylbenzidine (TMB) with hydrogen peroxide [1]. The CuNPs act as a catalyst in the reaction and enable the color change (from colorless to blue) to occur at room temperature in the presence of glyphosate.

The ability to perform this reaction at room temperature significantly improved the portability and time of analysis in comparison to previous colorimetric methods which required a 40 °C incubation period [2]. An LOD of 0.4 ppm was found via UV-vis detection, which is below the EPA limit of 0.7 ppm glyphosate in environmental water samples. The CuNPs were characterized by Fourier transform infrared spectroscopy (FTIR), dynamic light scattering (DLS) and field emission scanning electron microscopy (FE-SEM), confirming the successful synthesis and the excellent long-term stability of the CuNPs produced. This method allows for direct integration into a microfluidic format in combination with smartphone-based detection to yield a simple, portable and low-cost analytical method for the in situ detection of glyphosate in environmental samples.

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MONITORING OF CARCINOGENIC COMPOUNDS IN URINE USING A pH-SENSITIVE POLYMER-BASED MICROEXTRACTION METHOD COUPLED TO HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY AND FLUORESCENCE DETECTION

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The determination of biomarkers in urine is a powerful tool to assess the presence (or lack) of many diseases, like cancer or endocrine disrupting syndromes. Among the most common biomarkers, polycyclic aromatic hydrocarbons (PAHs), their monohydroxylated metabolites (OH-PAHs) and alkylphenols are of special interest. However, the analytical performance in urine is a difficult task due to the high complexity of the matrix. In this sense, efforts are shifted to the incorporation of more efficient materials (preferably biocompatible) in biomonitoring applications.

Polymer hydrogels, which are three-dimensional networks formed by polymers with a high amount of water, have been widely used within biomedical applications. Furthermore, this type of polymers can respond to external stimuli such as pH, temperature, or ionic strength, thus having an enormous potential ability for extraction approaches.

In this study, a pH-sensitive polymer based on poly(styrene-*alt*-maleic anhydride) is used for the first time for the determination of a group of PAHs, OH-PAHs and 4-n-nonylphenol in urine. The microextraction and preconcentration method based on the dispersion of the polymer in the urine followed by its insolubilization due to a change of pH. The microextraction method was successfully applied for the analysis of smoker and non-smoker human urine samples in direct combination with high-performance liquid chromatography [1].

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USE OF BIOPOLYMERS IN MINIATURIZED DISPERSIVE SOLID-PHASE EXTRACTION: SCREENING STUDY FOR POLYCYCLIC AROMATIC HYDROCARBONS

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Since the introduction of the Green Analytical Chemistry principles, there has been an increasing concern on the sustainability of analytical sample preparation approaches, particularly if considering they constitute the most time-consuming step of the method and the main source of laboratory wastes. Among the alternatives explored, it is important to highlight the miniaturization of the extraction methods, which has been accompanied by an intense research on greener and less toxic solvents and sorbents. Biopolymers emerge as potential candidates to be used as natural sorbents in microextraction schemes, given their biodegradability, versatility, and easily functionalization.

This study offers preliminary results on the use of several biopolymers (i.e. Chitosan, Alginate, Keratin) in dispersive micro-solid-phase extraction (µ-dSPE) in combination with ultra-high-performance liquid chromatography coupled to a fluorescence detector (UHPLC-FD), for the determination of fifteen priority polycyclic aromatic hydrocarbons (PAHs) as target compounds present in environmental waters, with the purpose of finding structures features among biopolymers justifying better analytical performance for these target PAHs. [1,2]

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DETERMINATION OF ULTRAVIOLET FILTERS IN HUMAN NAILS USING AN ACID SAMPLE DIGESTION FOLLOWED BY ULTRA-HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY ANALYSIS

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Ultraviolet filters (UV-filters) are specific chemicals that absorb and reflect UVA and UVB radiation from the sun. They are regularly used in sunscreens and in other personal care products (PCPs), and in products like plastics, adhesives, toys, or furniture finishes. This work develops and validates a new method to determine concentrations of UV-filters (BP-1, BP-2, BP-3, BP-6, BP-8, 4-OH-BP, THB, AVB) in human nail samples. Nails are easily available and are considered to be suitable indicators of cumulative and continued exposure to harmful chemicals. The treatment of nail samples includes microwave assisted digestion/extraction (MAE) in a methanolic solution of o-phosphoric acid (0.05 mol L^{-1}) followed by analyte determination using ultra-high performance liquid chromatography-mass spectrometry (UHPLC-MS/MS) in multiple reaction monitoring mode. The analytes were separated in less than 10 min. The digestion procedure was optimized using multivariate techniques. Matrix-matched calibration with a pig hoof matrix was used for validating the method. A study of accuracy with spiked blank samples was also conducted. The calculated detection limits varied between 0.2 and 1.5 ng g^{-1}, and quantification limits between 1.0 and 5.0 ng g^{-1}. The trueness of the method was an estimation of the recovery, which was between 90.2% and 112.2%; with an estimated precision (relative standard deviation, % RSD) lower than 12.3% for all UV-filters. Nail samples were obtained from 22 volunteers (male and female). The results showed that BP-1 and BP-3 mainly bioaccumulate in human nails.

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MOLECULARLY IMPRINTED POLYMERS FOR THE SOLID-PHASE EXTRACTION OF CATHINONES FROM RIVER WATER

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Owing to the specific recognition capability towards target analytes, the application of molecularly imprinted polymers (MIPs) has attracted great attention in sample preparation for environmental analysis [1]. In this study, a MIP were synthesized using ephedrine as template, methacrylic acid as functional monomer and ethylene glycol dimethacrylate as cross-linker. A highly selective and sensitive method for enantiomeric determination of 5 cathinones in river water using the optimized MIP as sorbent in the SPE followed by liquid chromatography coupled with high-resolution mass spectrometry was developed. SPE parameters affecting extraction efficiency and selectivity, such as the volume and pH of loading sample, and the type and volume of washing solution and elution solution, were investigated and optimized. The stereoselectivity of MIP sorbents towards the enantiomers of analytes during the SPE process was also investigated. With the optimal conditions, good recoveries of 68 - 83% with minor matrix effects of -6 - 2 % were obtained. The detection limits and quantification limits were between 0.3 - 0.8 ng/L and 1.0 - 2.0 ng/L, respectively. Finally, the developed method was successfully applied in the analysis of the river water samples and methedrone and butylone were detected at low ng/L.

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DEVELOPMENT AND VALIDATION OF A MULTIRESIDUE METHOD FOR THE ANALYSIS OF DIVERSE ORGANIC POLLUTANTS IN ATMOSPHERIC FINE PARTICULATE MATTER ($PM_{2.5}$)

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Exposure to atmospheric fine particulate matter with an aerodynamic diameter of less than 2.5 microns ($PM_{2.5}$) associated pollutants represents a global concern due to the risk posed in human health after introducing them into the organism by inhalation [1]. In the present study, a simple and sensitive method is developed for the simultaneous analysis of 50 organic pollutants, comprising 18 polycyclic aromatic hydrocarbons (PAHs), 12 phthalate esters (PAEs), 12 organophosphorus flame retardants (OPFRs), 6 synthetic musk compounds (SMCs) and 2 bisphenols because of their toxicity and ubiquity in the environment. The method consists of three cycles of ultrasound extraction and vortex (US + vortex) [2], followed by a vortex-assisted dispersive solid phase extraction (d-SPE) clean-up [3] and a final determination step by using programmed temperature vaporization-gas chromatography-tandem mass spectrometry (PTV-GC-MS/MS). Moreover, experimental conditions concerning clean-up adsorbents (alumina, silica gel and florisil) and filters (glass fibre, PTFE and nylon) were studied, selecting those that provided the best results attending to analytical recoveries and blank signals. Finally, the proposed method was validated in terms of linearity, limits of detection and quantification (LODs and LOQs), analytical recoveries and intra-day and inter-day precision by analysing a spiked composite $PM_{2.5}$ sample.

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POLYCYCLIC AROMATIC HYDROCARBONS ANALYSIS IN TEA INFUSIONS AND TEA BEVERAGES USING MEMBRANE ASSISTED SOLVENT EXTRACTION

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Tea infusions and tea beverages, aromatic drinks prepared by brewing dried leaves, flowers, twigs or buds of *Camellia sinensis*, are popular dietary beverages widely consumed by millions of people worldwide. The presence of theanine and flavonoids and catechin compounds in *Camellia sinensis* leaves gives significant health benefits [1]. However, tea leaves could also contain several hazardous compounds, such as polycyclic aromatic hydrocarbons (PAHs), as consequence of environmental pollution, tea leaves harvesting and manufacturing process. The aim of the present study was the optimisation of a simple, fast and “green” Membrane Assisted Solvent Extraction (MASE) procedure for the extraction/enrichment and isolation of 16 EPA priority PAHs and benzo(e)pyrene (BeP) from tea infusion and fruit/herbal tea beverages. Extracted PAHs have been separated and detected by high performance liquid chromatography coupled to a fluorescence detector (HPLC-FLD). Variables affecting MASE comprising extraction temperature and time, stirring rate, acceptor solvent (hexane) volume, organic modifier in the donor phase (methanol) volume, aqueous donor phase pH and ionic strength were simultaneously studied by applying a Plackett–Burman design (PBD) as screening method. Results showed statistical significance for acceptor solvent volume, extraction time and stirring rate, which were optimised by an orthogonal 2^3+star central composite design (CCD). Quantitative recoveries for all PAHs (within 78–116%) were obtained by using the optimized extraction conditions: 350 µL of hexane, extraction time of 70 min and stirring rate of 175 rpm. The MASE method has been found sensitive (LOQs < 43 ng L^{-1}) and precise (RSDs of <13%). Finally, the method has been applied to assess PAHs levels in several tea infusions and tea beverages.

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HIGHLY EFFICIENT REMOVAL OF NEONICOTINOID INSECTICIDES BY A FAMILY OF THIOETHER–BASED METAL-ORGANIC FRAMEWORKS

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Metal-organic frameworks (MOFs) are porous crystalline materials, with specific properties such as porosity, high surface areas, etc., that, among many other applications, have already proven greatly suitability in the removal of both inorganic and organic contaminants [1]. Multivariate-MOFs (MTV-MOFs) are a relatively new family of these materials, which combine different organic ligands with particular functionalities in the same framework decorating their channels [2]. Herein, we report the use of a family of five eco-friendly water-stable isoreticular MTV-MOFs, prepared from natural amino acids, as solid-phase extraction (SPE) sorbents for the removal of neonicotinoid insecticides (thiamethoxam, clothianidin, imidacloprid, acetamiprid and thiacloprid) from environmental samples. In the past, circumventing the impact of agrochemicals on aquatic environments has currently become a necessity for health and ecological reasons. Particularly, NEOs are a widely used type of synthetic pesticides that, despite some recent limitations [3], have widely spread throughout the world in the past decades, due to their extraordinary efficacy in pest control. However, such results also lie at the origin of important environmental alarms [3]. In this work, three of MTV-MOFs containing thioether-based residues have shown remarkable removal efficiency. Distinctly, the novel multivariate MOF $\{Sr^{II}Cu^{II}_6[(S,S)\text{-methox}]_{1.5}[(S,S)\text{-Mecysmox}]_{1.50}(OH)_2(H_2O)\} \cdot 36H_2O$ (1), containing narrow functional channels decorated with both $–CH_2SCH_3$ and $–CH_2CH_2SCH_3$ thioalkyl chains (from *L*-methionine and *L*-methylcysteine) exhibited the higher removal efficiency of the amino acid based MOF family, being capable to capture 100% of acetamiprid and thiacloprid in a single step as SPE sorbent (in less than 30 seconds). Moreover, single crystal X-ray diffraction was performed to unveil the interaction nature between sorbents and analytes as well as other characterization studies (such as powder X-ray diffraction, N_2 isotherms and thermo-gravimetric analysis). Other remarkable features were as follows: good precision (reproducibility below 10 %) and acceptable reusability (up to 10 cycles). To demonstrate the suitability of these new adsorbents to capture NEOs, isolation of proposed pollutants was tested in river water (achieving by (1) 60-100 % of removal in a single step). Such unusual combination of outstanding efficiency, great stability in environmental conditions and low-cost and simple synthesis in (1), places this material among the most attractive MTV-MOFs adsorbents reported until the date for removal of this type of contaminants.

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ZEOLITIC IMIDAZOLATE FRAMEWORK-8 DECORATED WITH GOLD NANOPARTICLES FOR SOLID-PHASE EXTRACTION OF NEONICOTINOIDS IN ENVIRONMENTAL WATER SAMPLES PRIOR TO THEIR QUANTITATION BY HPLC-DAD

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Synthetic insecticides like neonicotinoids (NEOs) have been popularized as pest controllers in vegetables , fruits and, in general, agricultural plants [1]. Due to their characteristics (persistence, hydrophilicity and widespread use), NEOs can be easily transmitted to environmental matrices, among others. In this regard, the use of novel MOF-based materials with sample pretreatment purposes [2] could be a useful alternative to more sophisticated analytical techniques (HPLC-MS/MS) for NEOs monitoring in complex matrices. In this work, a composite assembled with aminated zeolitic imidazolate framework (NH_2-ZIF-8) [3] as host support of gold nanoparticles (AuNPs) for solid-phase extraction (SPE) of NEOs in water samples is presented. The preparation of material was simple and it was based on the attachment of AuNPs onto the surface of metal-organic framework (NH_2-ZIF-8) taking profit of the strong interaction between the amino group and AuNPs. Several characterization techniques (including Fourier-transform infrared spectroscopy powder, X-ray diffraction, scanning/transmission electronic microscopy and surface area measurements) were used to investigate the resulting composite. Regarding the SPE protocol, several parameters influencing on the extraction performance were studied, for instance sampling, volume, composition of elution solvent and elution volume, among others. The analytes were determined via HPLC with diode-array detection after SPE protocol. Under the optimal conditions, satisfactory recoveries of five pesticides (thiamethoxan, clothianidin, imidacloprid, acetamiprid and thiacloprid) were obtained (70-112%) in real samples, while limits of detection achieved ranged from 0.06 to 0.12 $\mu g\ L^{-1}$. We have proved for the first time that MOF@nanoparticles materials can be considered as promising SPE sorbents for high efficient extraction of pollutants. These MOF based sorbents could expand the applicability of SPE as sample pretreatment, as well as of other SPE-based microextraction techniques, beyond the typical sorbents used until now.

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ACCUMULATION OF VOLATILE METHYLSILOXANES IN AQUATIC ECOSYSTEM FOOD WEBS AND POTENTIAL ENVIRONMENTAL RISK: A REVIEW OF PUBLISHED STUDIES

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Volatile methylsiloxanes (VMSs) are a class of organic compounds characterized by presenting a linear or cyclic Si-O backbone, saturated with methyl groups [1]. They are incorporated in a variety of products, particularly personal care products, being categorized as "high production volume chemicals" by the U.S. Environmental Protection Agency [2]. Due to their massive use, they are increasingly being detected in wastewaters. This can result in direct exposure to aquatic receptor media and indirect exposure through the food chain [3]. The proposed work combined the dispersed data present in a total of 69 studies regarding VMSs uptake and accumulation in aquatic ecosystems and risk assessment studies, allowing a more reflective understanding of VMSs behaviour in aquatic compartments. The bioaccumulation potential was analysed using different endpoints, including bioconcentration, bioaccumulation, biomagnification, trophic or food web magnification factors. While some studies indicated trophic dilution, others showed a potential biomagnification of VMSs (namely D4, D5 and D6) along food webs. Regarding risk assessment, most studies that applied a probabilistic approach concluded that there is a negligible risk in the aquatic environment, while those that used a deterministic approach indicated that cyclic VMSs (D3-D6) might present potential risk. However, further studies are needed to better understand the risks of VMSs in the environment.

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ANALYTICAL METHOD FOR THE DETERMINATION OF ANTIBIOTICS AND METABOLITES IN BIRD FECES

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In the last years, there is an increasing concern about the occurrence and fate of emerging pollutants in the environment. One group of these pollutants are antibiotics as resistance to antibiotics has become one of the biggest threats to world health. An increasing number of infections are becoming more difficult to treat, as antibiotics lose their effectiveness [1]. After absorption by animals or humans, these compounds are metabolized and excreted as metabolites or as parent compounds via urine and feces. As most of animal feces are applied as organic amendment in agriculture soils, their organic pollutants can be accumulated in soils. Then, they can contaminate surface and groundwater, be uptake by plants and animals, and even enter in human food chain [2]. In this work, an analytical method has been developed and validated for the simultaneous extraction and determination of 24 antibiotics and 2 of their metabolites in bird feces (*Ciconia ciconia* and *Larus fuscus*). Sample extraction was based on ultrasound-assisted extraction. Extract clean-up was based on dispersive solid-phase extraction. Box-Behnken experimental design was applied for method optimization due to the high number of experimental variables to optimize (type and amount of clean-up sorbent, extraction time, number of extraction cycles, type and volume of extraction solvent) and variety of target compounds. Analytical determination was carried out by liquid chromatography-tandem mass spectrometry with electrospray ionization (LC-MS/MS). Analytical quantification was carried out using matrix-matched calibration curves. Good recovery (mean: 63%) and precision (<19% RSD), was obtained. Method quantification limits were less than 15.6 ng g^{-1} dry matter for most compounds.

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CHECK OF THE NATURAL PIGMENTS IN HENNA AND JAGUA FOR FAKE DETECTION

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Temporary tattoos are a popular alternative to permanent ones, and can be included in the group of new cosmetics [1,2]. In recent times, the use of natural pigments from plants, such as famous henna tattoos and, more recently, jagua tattoos have emerged as an alternative. Henna contains lawsone or 2-hydroxy-1,4-naphthoquinone (HNQ) as an active ingredient, but nowadays natural henna is usually mixed with additives, mainly *p-phenylenediamine* (PPD), which is a potent sensitiser that is harmful to health [3]. Jagua contains geniposide and its bioactive compound, genipin, both of which can be potential new allergens in temporary tattoos [4]. The fact that they are sold on well-known websites available to everyone causes insecurity. In addition, most of these commercial products are not labelled and their regulations have not yet been formulated.

Therefore, it is necessary to devise suitable methodologies for the quality control analysis of these complex samples and to determine these active ingredients. Since there are still no analytical methods for several of these compounds, this first work focuses on the development of a method for the determination of the original matrices. The first results obtained to prove the authenticity of these types of inks according to their markers (HNQ in henna, genippin and geniposide in jagua) and their analytical characterisation by means of different chromatographic techniques are presented. Thus, possible fraud in products sold as natural henna can be uncovered.

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CHARACTERIZATION OF NATURAL TATTOOS AND DYES: TARGETED AND UNTARGETED ANALYSIS OF HENNAS AND JAGUAS

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Temporary tattoos can be included in the group of new format cosmetics [1,2] Until now, there has been little research on emerging natural pigment-based temporary tattoos and their constituents [3]. This study focuses on the characterization of natural henna and jagua tattoos in commercial samples. Sample manipulation and treatment are minimal to analyse natural pigments as they are marketed. The characterization of the active compounds is performed by ultra-high performance liquid chromatography coupled with quadrupole time-of-flight mass spectrometry (UHPLC-QTOF-MS). At the same time, a novel untargeted characterization is applied for this type of samples, searching for compounds ranging from the original ingredients to other additives of interest they may contain. The fact that these tattoos may also be a source of unlabelled allergens is also being considered [4,5]. This work showed that not all the 34 samples analyzed contained the characteristic active ingredients and, in addition, substances of different nature were found. Therefore, a rapid and high-throughput methodology has been developed for the identification of the components of these tattoos, providing a necessary approach for quality control or identification of suspicious substances.

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ENANTIOSELECTIVE DETERMINATION OF PHARMACEUTICALS IN COMPOSTED SLUDGE BY CHIRAL LC-MS/MS

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Chirality is a relevant topic in environmental pollutants such pharmaceuticals, but it is usually ignored in analytical methods for their determination. Enantiomers are optical isomers with identical physical-chemical properties, but they can suffer different biotransformation, bioaccumulation and have distinct effects in the organisms [1]. Most of the chiral compounds are provided in racemic forms but the enantiomeric fraction can be altered in a chiral environment, for example during biological processes in wastewater treatment plants. The resulting digested sludge is composted and can be used for agricultural soils, which can involve human health risks due to the presence, among other pollutants, of chiral pharmaceuticals. Accurate data of the presence of enantiomers should be considered for a proper risk assessment since they can affect living organisms in a different manner [2]. In this work, an analytical method has been developed for the simultaneous extraction and enantioselective determination of chiral pharmaceuticals from two groups: β-blockers (atenolol, metoprolol, propranolol) and antidepressants (fluoxetine, norfluoxetine, venlafaxine and metabolite O-desmethylvenlafaxine). Sample extraction was based on ultrasound assisted extraction followed by a dispersive solid phase extraction clean-up. Analytical determination was carried out by chiral liquid chromatography-tandem mass spectrometry with an electrospray ionization source. Enantiomeric separation was performed on a Chirobiotic V chiral column (250 mm x 2.1 mm i.d., 5 µm.) purchased by Sigma-Aldrich, using vancomycin as chiral selector. Moreover, the mobile phase consisted of 10 mM ammonium acetate (pH 4 formic acid adjusted):MeOH (2:98; v/v) under isocratic conditions. The method was validated in compost, with resolutions of enantiomers from 2.3 to 13.8, achieved in 20 minutes time analysis. Recoveries of most enantiomers where between 46-110 % and precision, expressed as relative standard deviation, was lower than 16% for all the compounds.

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DISPERSIVE LIQUID–LIQUID MICROEXTRACTION OF CADMIUM, MERCURY AND LEAD FROM MEDICINES PRIOR TO ICP OES DETERMINATION ACCORDING TO UNITED STATES PHARMACOPEIA

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A simple, sensitive and matrix effect free analytical method for simultaneous determination of Cd, Hg and Pb from drug samples (i.e., commercial dosage tablets) by inductively coupled plasma optical emission spectrometry (ICP OES) has been developed. According to United States Pharmacopoeia (USP) chapter 232 [1], those metals are considered elemental impurities from class 1 and they must be assessed in pharmaceutical production as well as in quality control evaluation. In order to increase the sensitivity of the analysis, a dispersive liquid-liquid microextraction (DLLME) [2] was performed and seven factors affecting analyte extraction were optimized by multivariate analysis. The optimized conditions for simultaneous DLLME of Cd, Hg and Pb were: DDTC concentration 1.0% w v^{-1}, 100 µL of toluene as extractant solvent, pH 6.0, vortex time of 3 min, centrifugation time of 2 min and a centrifugation speed of 3000 rpm. Before DLLME, microwave-assisted sample preparation of drug samples was performed using dilute nitric acid solution. When compared to conventional ICP OES analysis, DLLME improves limit of quantitation (LOQ) values on average 40-fold for all analytes, being 0.3, 1.8 and 1.6 µg L^{-1} for Cd, Hg and Pb, respectively. Consequently, LOQ values were significantly lower than LOQ values recommended by USP (i.e., ≤3, ≤18 and ≤3 µg L^{-1} for Cd, Hg and Pb, respectively [3]). Accuracy was evaluated by addition and recovery experiments following USP chapter 233 [3] recommendations in eight commercial drug samples. Recovery and RSD values were within the range of 90-110% and 1-9%, respectively.

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DISPERSIVE LIQUID-LIQUID MICROEXTRACTION BASED ON DEEP EUTECTIC SOLVENT FOR ELEMENTAL IMPURITIES DETERMINATION IN ORAL AND PARENTERAL DRUGS BY INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY

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A simple, fast, sensitive and green analytical method for the analysis of Cd, Co, Hg, Ni, Pb and V in oral and parenteral drug samples using inductively coupled plasma optical emission spectrometry (ICP OES) has been developed. According to United States Pharmacopoeia (USP), those metals must be reported in all pharmaceutical products for quality control evaluation (i.e., elemental impurities from class 1 and class 2A of USP chapter 232 [1]). To improve the analytical capabilities of ICP OES, a dispersive liquid-liquid microextraction (DLLME) was performed using a safe, cheap, green and biodegradable deep eutectic solvent (DES) as extractant solvent (a mixture of 1:2 molar ratio of decanoic acid and menthol) [2]. Under optimized conditions, the DES-based DLLME procedure obtained limits of quantitation on average 10 and 21-times lower than target limits recommended for drugs from parenteral and oral route of administration [3]. Accuracy was evaluated by addition and recovery experiments following USP recommendations for four oral drug samples in liquid dosage form and three parenteral drugs. Recovery and RSD values were within the range of 91-109% and 1-6%, respectively.

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COMBINING DISPERSIVE LIQUID-LIQUID MICROEXTRACTION WITH ORAL BIOACCESSIBILITY TESTING FOR RISK ASSESSMENT OF MICROPLASTIC CONTAMINANTED BEACH SAND

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The Unified Bioaccessibility Method (UBM) was employed for determining oral bioaccessibility of a group of dialkyl phthalate congeners and bisphenol A in beach sand contaminated with polyethylene microplastics. To handle the bioaccessible gastric and gastrointestinal extracts after the UBM protocol, dispersive liquid-liquid microextraction in combination with liquid chromatography and mass spectrometry (DLLME-LC-MS) was employed. The results indicated the release of the less hydrophobic compounds (i.e., dimethyl phthalate, diethyl phthalate, and bisphenol A) when the sample was contaminated at the 17 $\mu g \cdot g^{-1}$ level with microplastic pellets. Relative accumulation ratios higher than 1 were achieved for these compounds, indicating a certain degree of accumulation during digestion. However, the average daily intake values for children, that were corrected with the bioaccessible fraction, were below the tolerable daily intakes, thus demonstrating lack of health risk.

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MINIATURIZED AND MODIFIED QUECHERS METHOD WITH MESOSTRUCTURED SILICAS FOR FOOD CONTROL OF PYRROLIZIDINE ALKALOIDS IN AROMATIC HERBS

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Pyrrolizidine alkaloids (PAs) are natural plant toxins whose intake has been associated to liver damage, mainly causing hepatic veno-occlusive disease, which can lead to liver cirrhosis and liver failure. Recent food alerts have notified concerning high levels of these alkaloids in aromatic herbs and spices [1], highlighting their occurrence as an important food safety issue which needs to be addressed urgently, as maximum concentration levels of these contaminants have not yet been legislated. Nevertheless, the high complexity of food samples hinders the extraction and analysis of these compounds, which are subjected to matrix interferences. In this context, the QuEChERS procedure is a suitable strategy, as it involves simultaneous extraction and clean-up of samples. Moreover, the advantageous textural characteristics of ordered mesostructured silicas make them suitable as clean-up sorbents to isolate undesirable matrix interferences [2]. Accordingly, this work, proposes a modification of the original QuEChERS procedure by using different large pore SBA-15 type mesostructured silicas non-modified and modified with amino groups (NH_2) as dispersive clean-up sorbents for the multi-component extraction of 21 PAs from different aromatic herbs (rosemary, basil, thyme, savory and herbs de Provence). Sample extracts were analyzed with ultra-high performance liquid chromatography coupled to ion-trap tandem mass spectrometry (UHPLC-IT-MS/MS) with ESI in positive ion mode, achieving separation of analytes within 10.5 min. The original procedure was successfully miniaturized by reducing the amounts of sample (0.2 g), solvents (2 mL), clean-up sorbents (25 mg sorbent + 150 mg $MgSO_4$) and partitioning salts (0.65 g) employed, leading to an improved cost-effective and environmentally friendly microextraction method, which meets the Green Analytical Chemistry principles. Less matrix effects were observed using mesostructured silicas than with PSA. Additionally, best recovery values were achieved with SBA-15-NH_2, with values >70% for most of the analytes. Therefore, mesostructured silicas can be considered promising clean-up sorbents in sample preparation. Finally, echimidine, echimidine *N*-oxide, retrorsine, europine *N*-oxide and senecivernine *N*-oxide were the main PAs found in the samples analyzed.

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SUSTAINABLE EXTRACTION OF PROTEINS, PEPTIDES, AND PHENOLIC COMPOUNDS WITH MULTIFUNCTIONAL PROTECTIVE EFFECT AGAINST OXIDATION FROM AN APRICOT RESIDUE

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The apricot seed is a residue resulting from apricot processing [1]. It is not considered a valuable part of the fruit despite it presents a high content in proteins and polyphenols. Some authors have described methods for the extraction of proteins [1] or phenolic compounds [2] and have even observed antioxidant activity in the extracts. Nevertheless, these methods employed polluting reagents/solvents. This work proposes the development of a sustainable method based on the use of pressurized liquids and green solvents for the extraction of proteins and phenolic compounds. Additionally, the study of the antioxidant activity of the extracts, the effect of the enzymatic hydrolysis of extracts on this activity, and the identification of main compounds contributing to this activity was also approached. Box-Behnken experimental design was employed for optimizing conditions (extraction time, temperature and solvent composition) to obtain the highest extraction yield of proteins and phenolic compounds and the extracts with the highest radical scavenging capacity, capacity to inhibit the formation of hydroxyl radicals, reducing capacity, capacity to avoid lipid peroxidation, and capacity to reduce cancer cells proliferation. Moreover, extracts were hydrolysed by gastrointestinal digestion using alcalasa to evaluate the release of peptides with protective effects against oxidative damage. Different mathematical models predicted these conditions and enabled to evaluate the role of proteins, peptides, and phenolic compounds in the protection against oxidative damage. Analysis of extracts by high-resolution mass spectrometry enabled to identify these compounds.

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DETERMINATION OF CHIRAL DRUGS IN SEWAGE BY SUPERCRITICAL FLUID CHROMATOGRAPHY

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The presence of pharmaceuticals in the aquatic environment is recognized as worldwide concerning issue. Despite mass balances for a myriad of pharmaceuticals have been deeply investigated during last years, less information is available regarding the enantiomeric fractions of chiral drugs, marketed as racemates, in samples obtained from urban wastewater treatment plants. Spread of supercritical fluid chromatography (SFC) within analytical chemistry laboratories and development of interfaces between this technique and ESI-MS instruments have opened new perspectives for the efficient determination of chiral compounds in complex environmental matrices. In this presentation the effect of SFC conditions (including parameters related to separation and ionization steps) in the determination of a selection of quiral, basic drugs are discussed. Thereafter, the performance of selective extraction approaches, either based on mixed-mode or cationic exchange sorbents, for their concentration from wastewater and freeze-dried sludge is discussed. The final procedure achieved chiral separations of seven out of eight tested species within an analysis time of 15 min. The presentation summarizes the performance of the developed chiral methodologies, including accuracy and matrix effects assessment, and shows concentration data of tested compounds in water and solid samples obtained from urban STPs. Finally, their enantiomeric fractions in these matrices are calculated and compared with those existing in prescription drugs. For half of investigated compounds, enantiomeric ratios varied between environmental matrices and pharmaceutical preparations.

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SELECTIVE EXTRACTION AND DETERMINATION OF THE BIOCIDE CHLORHEXIDINE IN SLUDGE FROM URBAN SEWAGE TREATMENT PLANTS

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Chlorhexidine is a common biocide, included in the formulation of many personal care products. Owing to its large molecular weight, limited water solubility and poor degradability this compound is expected to accumulate in sludge at sewage treatment plants (STPs). Such behaviour might lead to concerning residue levels during sludge application as fertilizer in agriculture. Moreover, biocides are believed to have the potential to modulate the bacterial community existing in STPs, which might disturb the biodegradability of other pollutants during wastewater treatment [1]. The above evidences justify the development of effective analytical approaches enabling the fast and accurate determination of this biocide. Some specific features of chlorhexidine, such as its strong interaction with negatively charged compounds, non-polar character and trend to ionize as a mixture of single and double charge species merit to develop a tailored analytical approach.

This presentation discusses the parameters affecting the yield of matrix solid-phase dispersion (MSPD) as sample preparation technique for chlorhexidine extraction from freeze-dried sludge samples, it highlights the effect of the chromatographic column in the efficiency of LC separations and peak shape, and investigates the distribution of chlorhexidine in a selection of samples obtained from different urban STPs in the Northwest of Spain in two different years. Finally, environmental concentrations are compared to in-vitro toxicity thresholds obtained for different model microorganisms in order to better understand the potential environmental risks of chlorhexidine.

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ULTRA PERFORMANCE LIQUID CHROMATOGRAPHY-TIME OF FLIGHT MASS SPECTROMETRY TO DETERMINE FLUMEQUINE, DICLOFENAC AND THEIR MAIN METABOLITES IN MICE BIOLOGICAL TISSUES

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The use of lab-model animals to evaluate the biological response to environmental pollutants as well as their possible effects on humans, should be carried out through the design of lab experiments that mimic, as far as possible, the environmental conditions in which the pollutants are present. A usually way to achieve similar conditions to those found in the environment is the exposition to "chemical cocktails" [1,2]. Considering the above, the main idea of this work is to evaluate the metabolism of pharmaceuticals, one of the main groups of emerging pollutants. With this purpose, *Mus musculus* mice were used as lab-model mammals and subjected to "drug cocktails". The substances to be tested (diclofenac (DIC) and flumequine (FLUM)) were selected based on their toxicological and environmental interest. FLUM, DIC and their main hydroxylated metabolites (3-hydroxy, 4-hydroxy and 5-hydroxy diclofenac) were determine in plasma, brain, kidney and liver samples of model mice. Target analytes were identified and analysed by Ultra Performance Liquid Chromatography separation with Quadrupole Time of Flight Mass Spectrometry detection (UPLC-ESI-QTOF-MS). Several columns and different mixtures of organic solvents and aqueous solutions with additives were tested under isocratic and gradient elution profiles in order to achieve an efficient separation of the selected compounds. The separation was achieved on an Acquity BEH C18 column (50 mm × 2.1 mm i.d., 1.7 µm particle size) at 30ºC at a flow rate of 0.3 $mL \cdot min^{-1}$, using water (A) and methanol (with 0.1% (v/v) formic acid) (B) as mobile phase. The following gradient elution was applied: t=0 min 70% A; t=3.0 min 45% A; t=10 min 45% A; t=13 min 10% A; t=15 min 70% A and t=17 min 70% A. Detection was carried out with positive ionization in an electrospray source (ESI) at 2.0 kV capillary voltage, 120ºC for source temperature and 400ºC for desolvation temperature. The propose chromatographic method, provided good resolutions considering the similar structures and the same m/z values for the three hydroxylated metabolites of DIC, and unequivocal determination of the selected compounds with low limits of detection and quantification.

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CARRIER MEDIATED ELECTROMEMBRANE EXTRACTION (EME) FOR THE DETERMINATION OF NON-STEROIDAL ANTI-INFLAMMATORY DRUGS (NSAIDS) IN BIOLOGICAL SAMPLES

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Electromembrane extraction (EME), developed in 2006 [1], is a simple pretreatment technique based on the use of an electric field as driving force to promote a selective transfer of analytes from an aqueous donor solution to an aqueous acceptor solution across an organic solvent immobilized as supported liquid membrane (SLM). This technique allows reaching an excellent clean-up and high levels of sensitivity and selectivity in complex matrix samples. Up to now, most EME methods describe the use of pure organic solvents or mixtures as SLM. However, the need to incorporate carriers in the SLM to achieve the extraction of high polar compounds seems to indicate the presence of certain additives in the organic medium affect to the extraction yield [2]. In this work, it has been studied if the presence of a carrier in the organic solvent used as SLM may improve the extraction efficiency. Five widely used non-steroidal anti-inflammatory drugs (NSAIDs), salicylic acid (SAC), ketoprofen (KTP), naproxen (NAX), diclofenac (DIC) and ibuprofen (IBU) were selected as model analytes. EME was carried out using a home-made device designed with a flat configuration (FM-EME). NSAIDs were extracted from pH 5 donor solution (10 mL, not adjusted), stirred at 400 rpm, to pH 12 acceptor solution (250 µL, NaOH 0.01M adjusted) applying 80V for 12 minutes. The organic medium (1-octanol and 1-nonanol) was modified by adding different amounts of Aliquat®336, a cationic carrier commonly used in EME procedure for anionic compounds [3]. The results compared with those obtained in the same extraction conditions using the pure organic solvent as SLM, showed better extraction recoveries for all compounds at nearly all tested concentrations of Aliquat®336 which indicate the presence of a cationic carrier in the liquid membrane has a positive effect in the extraction of anionic compounds. Best results were achieved when 1-nonanol was modified with 2.5% (w/v) Aliquat®336, with extraction recoveries within the range of 39 and 53%. Detection and quantitation limits were within 0.02-1.0 ng mL^{-1} and 0.05-3.0 ng mL^{-1}, respectively. The analyses were carried out by high performance liquid chromatography (HPLC) with diode array (DAD) and fluorescence (FLD) detection and finally applied to the analysis of human urine samples.

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DISPERSIVE LIQUID LIQUID MICRO EXTRACTION FOR RAPID DETERMINATION OF DRUGS FACILITATED SEXUAL ASSAULTS IN URINE BY LC-MS/MS

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The process of dispersive liquid liquid micro extraction technique (DLLME) was successfully applied for the simultaneous extraction and subsequent high performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS) determination of several classes of drugs facilitated sexual assault (DFSAs) from urine samples. Main drugs such as Alprazolam, Amitriptilina, Bromazepam, Clonazepam, Diazepam, Escitalopram, Flunitrazepam, Ketamine, Lormetazepam, LSD, MDEA, Methamphetamine, Midazolam, Norfentanil, Norketamine, Oxazepam, Trazodone, and Vanlafaxine were effectively extracted in single step and determined under the satisfactory selectivity, sensitivity, accuracy and precise and linearity. The matrix effect was very high for most of the analytes (maximum 98% ion suppression), which was effectively compensate by using the standard addition calibration technique. The limit of detections (LODs) varied from 0.00006 to 0.06290 µg mL^{-1} [limits of quantifications (LOQs) from 0.00019 to 0.20966 µg mL^{-1}]. Accuracy and precision were satisfactory and relative standard deviation percentage (RSD %) of intraday spanned from 2 – 15% and interday spanned from 2.4 – 19%. Intraday and interday recoveries were within the 64 – 99% and 65 – 106% ranges, respectively. Selectivity was analyzed by using blank urine sample and it proved that method was highly selective. The developed method was successfully applied to analysis of twelve urine samples from forensic cases, and the presence of Ketamine was detected/quantified in two cases, Lormetazepam in one case, LSD in two cases, Midazolam in three cases, Nordiazepam in five cases, Norketamine in two cases, and Ventafaxine in two cases. The proposed method was found to be high sensitive, high selective and accurate and precise for DFSAs assessment in urine samples

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AUTOMATIC ROBOT FOR PREPARATION OF ORGANIC SAMPLES (ARPOS)

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Gylphosate (N-phosphonomethyl) glycine) is one of the most widely used herbicides in the world. Due to its widespread use and interaction with the environment, both glyphosate and its main metabolite AMPA ((amminomethyl) phosphonic acid) were included in European legislation as substances subject to review as possible priority dangerous substances[1]. These two compounds (glyphosate and AMPA) are highly polar substances, so in order to be adequately analyzed and to reach the quantification limits established by the legislation, a derivatization of the sample must be carried out using FMOC (fluorenylmethyloxycarbonyl chloride) to achieve good chromatographic separation[2] [3] [4]. For this reason, there is a need to automate this derivatization process since it is a completely manual process and currently there are a high number of water samples that require to analyse glyphosate and AMPA. Labaqua, in collaboration with GERSTEL, has developed a robot that get to automate this derivatization process, eliminating in this way most of the manual process for glyphosate and AMPA analysis, therefore this automation increases considerably the productivity of the analysis. ARPOS is capable of adding all the derivatization reagents, as well as homogenizing and incubating the sample in a fully automatic way, so that the sample is ready for direct analysis by HPLC-MSMS. By means of a validation of the process carried out in Labaqua, its repeatability and reproducibility has been demonstrated, achieving a high profitability of the process. Furthermore, thanks to the great versatility of the ARPOS robot, analysis that involve manual processes such as soil extraction or LLE extraction will be able to be automated soon. Therefore, ARPOS robot is presented as a bet on the future for the automation of large-scale sample analysis.

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DISPERSIVE SOLID-PHASE EXTRACTION OF PHTHALIC ACID ESTERS FROM WATER SAMPLES USING A SELF-IMMOLATIVE POLYMER

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During the last decades, the production and use of plastics has highly increased generating important amounts of waste every year that, in combination with its inadequate management, results in a constant release of these materials into the environment [1].

In the Analytical Chemistry field, polymers play a very important role. In particular, some of them are successfully used as selective and efficient sorbents in solid-phase extraction (SPE) procedures. Though the amount of plastic waste produced in SPE is not high, the use of polymers is indeed an additional contamination source that could be reduced with a proper management and also by the eco-design of the materials. Self-immolative polymers (SIPs) are a class of polymers characterised by their capability of disassembling in a domino typo mechanism under suitable external stimulus (biological, physical or chemical). Thus, if properly designed, SIPs could contribute to the development of sustainable analytical methodologies in which environmentally unharmful immolation products are obtained [2]. In this work, a new SIP has been synthesized and characterized by different techniques. Its applicability as sorbent to the extraction of a group of phthalic acid esters (PAEs) from water samples in a µ-dSPE procedure has been explored, using gas chromatography coupled to a mass spectrometer for their determination. Different vias of immolation have also been tested in order to obtain the most efficient mechanism possible.

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SA-DLLME FOR THE SELECTIVE EXTRACTION OF SILVER NANOPARTICLES FROM TAP WATER

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According to the International Organization for Standardization (ISO), a nanoparticle (NP) is defined as a nano-object with all external dimensions in the nanoscale (1 nm to 100 nm) [1]. These nanomaterials (NMs) exhibit extraordinary properties compared to their bulk material analogous. Due to this, they have arisen particular interest in recent years. Silver nanoparticles (AgNPs) are the most widely used NPs especially due to the antimicrobial effects, and they may be considered one of the most important NMs. They are extensively used in medicine, healthcare products, the food industry and cosmetics, among others. Thereby human exposure to AgNPs is continuously growing. In addition, the release of silver from nanotechnology-based consumer products into the environment has already been showed in previous studies [2]. Such widespread use has led to concerns about the possible toxic effects of AgNPs and thus, safety of nanosilver needs to be established. In this communication, a new strategy for the selective extraction of AgNPs from tap water samples is proposed. The method combines surfactant assisted dispersive liquid liquid microextraction (SA-DLLME) with single-particle inductively coupled plasma mass spectrometry (SP-ICP-MS) determination. Experimental parameters affecting the efficiency of SA-DLLME, such as volume of surfactant/extractant mixture, vortex time, speed of vortex, centrifugation time and speed of centrifugation were investigated. Results showed that the optimal conditions were 1.0 mL of surfactant/extractant (49:1) mixture, 0.5 min vortex time at 1500 rpm and 5 min at 3500 rpm for the centrifugation step. The operational simplicity, low cost and less consumption of organic solvents make SA-DLLME a green choice. Yet, inorganic NPs still present detection challenges.

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MASE AS AN EXTRACTION PROCEDURE FOR ASSESSING CHEMICAL SUBMISSION SUBSTANCES IN URINE

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Chemical Submission (CS) refers to 'the substance administration to a person without his/her knowledge to cause him/her a change in the alertness, state of consciousness, and judgment' [1]. The term, that derives from the French "soumission chimique", was firstly used by Poyen et al. in 1982 [2]. Although CS includes all crimes related to this activity, a new term has arisen due to the high incidence of sexual assaults with drug use, Drug-Facilitated Sexual Assault (DFSA). The drugs involved in DFSA cases, commonly known as "date rape drugs" or "predatory drugs", include ethanol, streets drugs and traditional drugs of abuse and medicinal drugs, mostly benzodiazepines. Most of them are usually tasteless, odorless and colorless, orally administrated and activated at low doses. The determination of these drugs and their metabolites is challenging from the toxicological point of view as they are rapidly absorbed, metabolized and eliminated from the body within few hours after ingestion. Because urine provides a longer window of detection its analysis is preferrable over other biological samples analysis, as blood or head hair analysis. In this communication, a new strategy coupling Membrane Assisted Solvent Extraction (MASE) with HPLC-MS/MS for the selective extraction of chemical submission substances from urine samples is proposed. Comprehensive investigation of the extracting parameters affecting the efficiency of MASE procedure, such as organic solvent or pH, was carried out. Results proved that MASE extraction technique was suitable for the efficient extraction of the drugs under study. In addition, the reduction on the consumption of organic solvents as well as the miniaturization, make MASE an environmentally friendly procedure.

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ASSESSMENT OF VOLATILE METHYLSILOXANES AND SYNTHETIC MUSKS COMPOUNDS IN ORGANIC WASTE-BASED FERTILISERS – A FIRST APPROACH

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Agricultural production currently depends on non-renewable mineral resources and synthetic raw materials for maintaining and enhancing soil fertility. This linear economy model is quickly depleting natural resources while impacting the long-term quality of arable land, hence new fertilizer solutions based on organic materials and by-products are being encouraged. The use of organic waste-based fertilizers contributes to a circular economy model, transforming biodegradable wastes as sewage sludge, animal manure, or agricultural and food industries residues, into a value-added product [1]. But the occurrence of organic pollutants in these recycled raw materials requires further studies to ensure the safety of the final goods, since the elimination of hazardous chemicals is not guaranteed during production. Volatile methylsiloxanes and synthetic musks are two emerging contaminant classes of compounds quantified at high concentrations in sewage sludges and possible to occur in other matrices to be used in this type of fertilizers [2, 3]. In this work, a first approach for the determination of siloxanes and musks in commercial samples of organic waste-based fertilizers was assessed. A QuEChERS-GC/MS analytical methodology, based on solid-liquid extraction followed by a dispersive solid-phase clean-up step, previously employed for the analysis of sewage sludges, was tested and validated for that purpose. Results revealed the occurrence of both classes of pollutants. The predominant musk compounds were galaxolide (HHCB) and tonalide (AHTN), while for siloxanes all cyclic congeners were present at relevant concentrations, mostly D4 and D5, followed by D6.

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DETERMINATION OF POLYCHLORINATED BIPHENYLS IN WATER SAMPLES BY USING CYCLODEXTRIN-SILICA MATERIALS

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Polychlorinated biphenyls (PCBs) are ubiquitous environmental pollutants whose wide industrial use has been banned over the years in most countries due to their persistence and trend to bioaccumulate. In fact, the International Agency for Research on Cancer defined them in 2016 as carcinogenic to humans based on sufficient evidence of an increased risk of cancer.

A new method for the determination of six PCB-congeners (PCB28, PCB52, PCB101, PCB138, PCB153, and PCB180) in environmental water samples has been developed. Given the fact that the formation of inclusion complexes between PCBs' molecules and cyclodextrins has been already studied [1], the use of a cyclodextrin-containing silica microparticulated material [2,3] in solid-phase extraction is proposed in order to improve the sensitivity and selectivity of the method.

The developed method allows quantifying PCBs at very trace level, with limits of detection reaching concentrations between 0.2 and 1.7 ng L^{-1}. Other analytical parameters such as the repeatability, with coefficients of variation lower than 11%, were also established. To end, six real water samples were analyzed and results were compared with those obtained by applying a reference method. The proposed methodology can be utilized for evaluation and remediation purposes.

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EXTRACTING ANTIBIOTICS FROM WATER WITH A CYCLODEXTRIN-MODIFIED POLY(GLYCIDYL-CO-ETHYLENE DIMETHACRYLATE) HYBRID SORBENT

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A non-adequate treatment of water can have a variety of consequences. Among them, the presence of pharmaceuticals in the environment, including drinking water, is one of the most significant [1].

A procedure for the solid-phase extraction of fluoroquinolones (enoxacin, ofloxacin, norfloxacin, ciprofloxacin, and sparfloxacin) in water has been developed. The sorbent used is based on a poly(glycidyl-co-ethylene dimethacrylate) network, whose previously modified surface has been functionalized with γ-cyclodextrin. The optimization of the extraction methodology shows good intra-day and inter-day repeatability of the extraction procedure, with coefficients of variation between 2.5 and 5.1% and the possibility of reusing the material. The detection limits of the method have been established at the µg L^{-1} level, confirming thus the possibility of quantifying trace levels.

The proposed material can be used for assessing the presence of antibiotics in aqueous environments through an extraction procedure taking advantage of the presence of γ-cyclodextrin [2] on its structure.

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EVALUATION OF THE USE OF DEEP EUTECTIC SOLVENTS (DES) FOR THE SELECTIVE SEPARATION OF BIOACTIVE CARBOHYDRATES

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Currently, the interest in the extraction of carbohydrates (CH) from inexpensive and renewable raw materials is increasing for their potential use in different areas such as biorefinery, pharmaceuticals or food industry. Some CH may exert different bioactive properties, such as prebiotic disaccharides (i.e. lactulose) or polyalcohols (i.e. inositols, with an important role in insulin-related diseases). However, bioactive CH obtained from natural products are usually co-extracted with other sugars, which could interfere in their bioactivity, making the fractionation of the extracts mandatory. This is a challenging process considering their similar structures and concentrations. The low selectivity of conventional solvents has led to research into the development of new alternatives, such as supercritical fluids, ionic liquids or deep eutectic solvents (DESs). These last solvents are eutectic mixtures constituted by two or more compounds acting as either hydrogen bond donors or hydrogen bond acceptors, which have proven to be selective for the extraction of specific compounds and environmentally friendly [1]. Despite their interesting properties, the usefulness of DES for the extraction or fractionation of CH of low molecular weight is practically unexplored. In this work, the solubility of 10 sugars (glucose, fructose, galactose, lactose, sucrose, lactulose, maltose, trehalose, *myo*-inositol and mannitol) in 3 chloride-coline based DES (ChCl:EtGl 2:1, ChCl:Gl 2:1, ChCl:Oxh 1:1) at two different temperatures (25 and 45°C) was evaluated. The DES that provided the best results was applied to the selective fractionation of bioactive CH from other sugars in 1:1 (w/w) binary mixtures. The analysis of CH was performed by HPLC-MS, using a BEH amide column. In general, monosaccharides were the most soluble CH in all DES tested, while polyalcohols were the least. Regarding disaccharides, sucrose and lactulose were the most soluble sugars. As for DES, the most stable mixtures were ChCl:Gl and ChCl:Oxh, since precipitation was observed in ChCl:EtGc after a week of storage. On the other hand, ChCl:Oxh, although stable, was observed to degrade sugars at 45°C, especially lactulose. Then, the efficency of selected DES were evaluted for the selective fractionation of CH binary mixtures. These results show DES as promising environmental friendly solvents for this fractionation process and suggest the interest of further investigation in this field.

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USE OF MESOPOROUS SILICA MATERIAL WITH GOLD NANOPARTICLES AS SORBENT FOR ORGANOCHLORINE PESTICIDES PRECONCENTRATION FROM WATER SAMPLES

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Nowadays, pesticides are widely used not only in agriculture but also in many areas of life. Due to their resistance to environmental degradation, they have become one of the most concerning organic micropollutants. Among them, organochlorine pesticides (OCPs) have been used for more than a half century for pest and insect control [1,2].

In this work, a novel sorbent, based on UVM-7 mesoporoses silica doped with Au nanoparticles, has been proposed for organochlorine pesticides determination. Cartridges containing this material has been applied to the extraction and preconcentration of pesticides from water samples, through a solid-phase extraction (SPE) protocol, with their later determination by gas chromatography coupled to an electron capture detector. First, UVM-7 materials were properly characterized by electron microscopy, porosimetry and X-ray diffraction, thus confirming their structure and Au attachment. After the optimization of main extraction parameters, recoveries above 60% were obtained for all analytes and in the range of 80-110% for most of them, with enrichment factors in the range of 247-472. The obtained sensitivity was comparable with other reported methods, with limits of quantification in the range 0.3-20 ng L^{-1}, thus allowing the determination of these compounds according to European legislation. The developed method has been successfully applied to the analysis of real spiked samples in comparison with a reference method, thus being this sorbent an alternative for organochlorine pesticides enrichment, through a simple, reusable, cheap and environmentally-friendly SPE procedure.

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DETERMINATION OF ENDOCRINE DISRUPTING CHEMICALS IN URINE USING A HYBRID CYCLODEXTRIN MESOPOROUS SILICA MATERIAL AS SORBENT

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Exposure to parabens and bisphenols is very common in current human populations, since these chemicals are present in several everyday use products, including cosmetics, personal care, processed food, plastics, drugs, etc. These compounds are proved to modify the normal endocrine functions when are in constant contact with the body for long periods, thus being considered as endocrine disrupting chemicals. Among them, bisphenol A (BPA) has received a special attention in the last decades due to its widely use and its potential risk for human health [1,2].

In the present work, a method for the determination of parabens and bisphenol A in urine samples has been developed. For this, hierarchical mesoporous silica doped with β-cyclodextrin was developed and used as sorbent for preconcentration and clean-up step, prior to analyte determination by liquid chromatography coupled to mass spectrometry detector. Non-ordered silica materials were also synthesized for comparison. All materials were characterized and the attachment of cyclodextrins has been proved as well as their uniform distribution in the resulting material. After protocol optimization, good analytical parameters were achieved, including recoveries in the range of 96-109% for all analytes, as well as limits of quantification below 0.2 µg L^{-1} in all cases. The developed method was applied to the determination of parabens and BPA in real urine samples in comparison with a reference method, being BPA the most detected analyte.

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EXTRACTION OF BIOACTIVES COMPOUNDS FROM *SILYBUM MARIANUM USING GAS EXPANDED LIQUID EXTRACTION*

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For over then 2000 years, Milk thistle has been used as one of the most important medicinal plant as a remedy for liver disease. It has also been reported to have anti-tumor, anti-aging, anti-diabetic, cardioprotective and neuroprotective effects [1]. In 2019, milk thistle seed products placed in the 10th and 23rd in U.S. natural channel and U.S. mainstream multi-outlet sales with more than $26 million[2]. The aim of numerous studies has been to improve novel and efficient extraction techniques to produce high-quality extracts respecting the Green Chemistry Concepts. Among them, Gas-Expanded Liquids (GXLs) are the mixture between liquid solvents and pressurized compressible gas such us CO2 [3]. Thus, the objective of this work was to develop and evaluate the CO2 –expanded liquids (CXLs) as a new and green promising method for the extraction of bioactives such as Silymarin from Silybum marianum. Extraction solvent consisted on mixtures of CO 2 -Ethanol-water under different conditions, besides kinetic study was evaluated. The best yield reached 55.97% using a ternary mixture of solvents composed by Ethanol:CO2:H2O (60:25:15) at 40C° and 90bar in 160min. Moreover, the extracts obtained have been chemically and functionally characterized. HPLC-ESI-MS/MS (triple quadrupole) and in-vitro assays such as the anti-inflammatory and anti-cholinergic activities respectively.

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HIGHLY STABLE SUPRAMOLECULAR SOLVENTS FOR LIQUID-LIQUID EXTRACTION

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Supramolecular solvents (SUPRASs) are nanostructures liquids obtained by self-assembly of amphiphilic compounds that have been extensively used in extraction processes due to their ability to solubilize a wide variety of analytes by establishing different types of interactions, their high number of solubilization sites and their capacity to disperse in samples favoring analyte transfer from sample to solvent [1]. However, their use in liquid-liquid extraction is limited by the need to maintain self-assembly conditions during extraction to keep the integrity of SUPRASs. The research here presented focuses on the development of supramolecular solvents that are highly stable in aqueous media and can therefore be used in liquid-liquid extractions without maintaining their formation conditions. The new solvents were synthesized from aqueous solutions of alkyl phosphonic acids ($C_nH_{2n-1}\text{-}PO_3H_2$, n=6-12) and tetrahexylammonium chloride ($(C_6H_{13})_4NCl$) under pH conditions where the former are in their amphoteric form (alkyl hydrogen phosphonates, $C_nH_{2n-1}PO_2H^-$). Under these conditions, the spontaneous formation of nanostructures consisting of aggregates of $C_nH_{2n-1}PO_2H^-$ together by $(C_6H_{13})_4N^+$ bridges occur spontaneously. The nanostructures form coacervate droplets which separate from the bulk solution as a second liquid phase less dense than the equilibrium solution. The phase diagrams for the formation of the SUPRASs and the dependence of the composition and volume of the solvents formed on the concentrations of alkyl phosphonic acid and tetrahexylammonium chloride used for their synthesis have been established. Studies on the stability in water of SUPRASs with different compositions have revealed that it augments with increasing the length of the hydrocarbon chain of the alkyl phosphonic acid while it is independent of the $C_nH_{2n-1}PO_2H^-/(C_6H_{13})_4N^+$ ratio in the SUPRAS. The stability of the SUPRASs also increases with the ionic strength of the aqueous sample. The applicability of the newly developed SUPRASs in liquid-liquid extraction processes was demonstrated by the extraction of polycyclic aromatic hydrocarbons from aqueous samples using a SUPRAS of decyl phosphonic acid. Recoveries near 100% and preconcentration factors of c.a. 200 were obtained for all the analytes investigated.

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SUPRAMOLECULAR SOLVENT-BASED MICROEXTRACTION OF OXY-PAHS FROM FOOD

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Supramolecular solvents (SUPRAS) are nanostructured liquids formed by the self-assembly of amphiphilic aggregates with multiple binding sites and microenvironments of different polarity for efficient extraction at low volumes. [1] In this study, we have investigated the suitability of supramolecular solvents (SUPRAS)-based microextraction for the development of generic and fast sample treatment of solid foods prior liquid chromatography and high resolution mass spectrometry (LC-MS-QTOF) for the determination of oxygenated PAHs (oxy-PAHs). Oxy-PAHs have been scarcely studied in food despite the growing concern about their presence in these matrices due to their toxicity. In order to provide a green extraction method, the SUPRAS was made up of short/medium chain length alcohols (C_6-C_{10}) in mixtures of water and a sustainable solvent (methyl-tetrahydrofuran). These amphiphilic compounds of low toxicity and volatility are approved for use in food and cosmetics. The following variables were optimized in term of extraction efficiency and matrix effects: alcohol chain length and organic solvent percentage for SUPRAS production and sample amount. Mussels and chicken samples were used for optimization and validation. Total recoveries varied in the range 94-108% (RSD:7-14%) for mussels and between 89 and 95% (RSD: 3-12%) for chicken. The method provided quantification limits of 3 ng/g with low consumption of reagents (200uL of SUPRAS per sample) and it was based on simple agitation and centrifugation steps without concentration/evaporation. It was applied to several meat and fish-based processed food bought in local supermarkets in Spain. Low contamination levels (few ng/g) of oxy-PAHs were found in samples in a range 3 – 7.3 ng/g.

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OCCURRENCE OF ANTICANCER DRUGS IN AN URBAN WASTEWATER TREATMENT PLANT

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The International Agency for Research on Cancer predicts that its incidence will increase approximately 40% from 2018 to 2040, which will result in around 16.3 million deaths by the year of 2040. The anticancer drugs are medicines administered for the treatment of cancer. These pharmaceuticals are highly toxic and not specific for damaged cells, meaning that they also interfere and affect healthy tissues. After being consumed, part of them is excreted by the human body to the water cycle and, if not properly degraded in the wastewater treatment plants (WWTPs), they may end up in surface waters [1].

An analytical methodology, comprising liquid-liquid extraction and liquid chromatography-tandem mass spectrometry analysis, was successfully developed and validated for the identification and quantification of 14 anticancer drugs in wastewaters. This method was applied to the analysis of influents and effluents from one WWTP located in the northern Portugal. Flutamide, paclitaxel and cyproterone were not detected in any sample. All the other anticancer drugs were detected at least once, mycophenolic acid being found at highest concentrations in the influents (up to 1585±54 ng/L). After primary, secondary and tertiary (UV) treatments, 5 anticancer drugs were still detected in the effluents: bicalutamide, capecitabine, mycophenolic acid, cyclophosphamide and ifosfamide. Nevertheless, using the risk assessment approach, it was concluded that bicalutamide, capecitabine, cyclophosphamide and ifosfamide may not be posing aquatic biota at risk. On contrary, mycophenolic acid showed a possible high risk to aquatic organisms [2].

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EVALUATION OF DIFFERENT CHOLINE-BASED DEEP EUTECTIC SOLVENT FOR METAL EXTRACTION IN MUSSEL SAMPLES

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Deep eutectic solvents (DES) are an emerging class of green solvents based on a mixture of a hydrogen bond donor and acceptor [1]. When compared to conventional inorganic and organic media (e.g. volatile organic solvents, highly acidic solutions, etc.), DES offer unique characteristics such as tunable physicochemical properties, biodegradability, non-flammability, low toxicity and cost, etc. Several authors have recently showed that DES could be employed as an efficient media in sample digestion and extraction treatments for elemental in atomic spectrometry [2,3] Therefore, the aim of this work is to explore the benefits and drawbacks of different choline-based deep eutectic solvent for metal extraction in mussels samples. To this end, extraction conditions have been optimized by experimental design and then sample extracts have been analyzed by means inductively coupled plasma optical emission spectrometry (ICP-OES).

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DETERMINATION OF ELEMENTAL BIOAVAILABILITY IN SOILS AND SEDIMENTS BY MICROWAVE INDUCED PLASMA OPTICAL EMISSION SPECTROMETRY (MIP-OES): MATRIX EFFECTS AND CALIBRATION STRATEGIES

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Elemental bioavailability studies of soils and sediments in environmental sciences are commonly developed by single step or sequential extraction procedures with different inorganic extractant solutions (e.g. acids, salts, etc.) [1] followed by a detection step by means atomic spectrometry techniques, particularly inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) due to their multielement capabilities and figures of merit [2]. In the past few years, microwave induced plasma optical emission spectrometry (MIP-OES) has generated a great interest as an alternative technique to ICP-OES for elemental analysis. Detection capabilities afforded by current MIP-OES instrument are close to those obtained with ICP-OES but with a significant reduction of operational cost due to the use of nitrogen as plasma gas instead of argon. Nevertheless, this plasma source still suffers from severe matrix effects due to easily ionizable elements (i.e., Na, Ca, etc.) [3,4], precisely the concomitants naturally present in extractant solutions for elemental bioavailability studies (e.g., $MgCl_2$, NaOAc/HOAc buffer, etc.). Thus, the aim of this work is to evaluate the feasibility of MIP-OES as a detector for elemental bioavailability studies in soils and sediments. To this end, the influence of MIP-OES operating conditions and wavelengths characteristics on the analyte emission for 15 elements (As, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Rh, Se, Sr and Zn), operating different extractant solutions widely employed for such kind of studies (e.g., $MgCl_2$, $CaCl_2$, HOAc, EDTA, $NaNO_3$, NaOAc/HOAc and $NH_2OH{\cdot}HCl$), was evaluated. Next, different calibration strategies based on internal standardization (e.g., spiked internal standards and plasma molecular emission bands) were evaluated to correct non-spectral interferences and instrument signal drift. Finally, MIP-OES was applied to study the elemental bioavailability in sediment samples from an area affected by mining waste and soil samples from a vineyard affected by copper-based fungicides.

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NON-DESTRUCTIVE EXTRACTION AND CHARACTERIZATION OF PLATINUM NANOPARTICLES FROM ENVIRONMENTAL FILTERS BY MEANS ICP-MS OPERATING IN SINGLE PARTICLE MODE

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Platinum nanoparticles (PtNPs) are widely employed as catalysts in the petrochemical and the automotive industry and, hence, they may be released to the environment affecting air quality and human health [1,2]. The analysis of atmospheric particulate matter is usually carried out by aspirating air through a microquartz-containing cellulose filter followed by a gravimetrical weighting [1,3]. As regards NPs, a microwave-assisted digestion of the filters followed by an elemental analysis step by means inductively coupled plasma mass spectrometry (ICP-MS) determination is usually employed [1]. Unfortunately, operating this way, information of NPs characteristics (size and composition) and concentration is lost. Therefore, it its important to develop new procedures for PtNPs characterization in atmospheric filters. On this regard, ICP-MS operated in single-particle mode is a promising technique for such kind of applications since it allows NPs determination and characterization in complex samples. Therefore, the aim of this work is to evaluate different non-destructive extraction procedures for PtNPs determination in air filters by means single-particle ICP-MS. To this end, three extraction procedures were tested, namely: (i) direct immersion; (ii) Nespresso-assisted hard cap extraction [4]; and (iii) ultrasound-assisted extraction. Experimental extraction conditions (e.g. type and concentration of extractant, extractant volume and extraction time) were optimized by means experimental design. Experimental results showed that none of the strategies employed affords quantitative PtNPs recovery from air filters. The best approach was ultrasound-assisted extraction (i.e. 50 minutes of extraction and 40 mL of 1.4% w w^{-1} ammonium hydroxide solution) which allow an extraction efficiency of 82 ± 5%. For the remaining strategies, recoveries were below 50%. Further research is required for improving NPs extraction from air filters.

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AN EFFECTIVE ANALYTICAL APPROACH TO DETERMINE SYNTHETIC OPIOIDS IN ORAL FLUID SAMPLES

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Novel synthetic opioids have been appearing on recreational drug markets in the last years. It is becoming a global threat to public health and safety. In particular, fentanyl and non-pharmaceutical fentanyl are related in overdoses fatalities in the United States in last decades [1]. These compounds are used as adulterants in heroin and other opioids, or standalone products. Since 2009, 57 new synthetic opioids have been detected in Europe's drug market, according to the EMCDDA 2020 report, which includes eight first reported in 2019 [2]. Recent data show increasing overdose deaths involving fentanyl and fentanyl analogs over 16 % from 2018 to 2019, meaning that in 2019, more than 36,000 overdose deaths involved synthetic opioids [3]. High sensitivity analytical methods are required for the detection of fentanyl and compounds derived from fentanyl, since these compounds are found in low concentrations in biological matrices. In this work, a simple and effective analytical approach based on fabric phase sorptive extraction (FPSE) [3] is proposed for the analysis of 11 synthetic opioids in oral fluid samples. The most important factors were evaluated to achieve the optimal extraction efficiency. Sample volume, extraction time, shaking mode, desorption solvent volume, and sample pH were evaluated. Furthermore, the type of coating of the FPSE phase (Carbowax 20M) and the desorption solvent (ethyl acetate) were evaluated before the use of an experimental design. Then, method validation was performed in terms of linearity, precision and accuracy showing satisfactory results.

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NOVEL MIXED MODE ZWITTERIONIC SORBENTS FOR THE DETERMINATION OF CONTAMINANTS IN COMPLEX WATER SAMPLES

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Complex samples require selective sample treatments, mainly to reduce the matrix effect that arises when using liquid chromatography and mass spectrometry-based detection (LC-MS). One way to overtake this problem is using selective sorptive extraction techniques, and in this case, the selectivity arises from the material. Mixed-mode ion-exchange sorbents can retain non-charged compounds through hydrophobic interactions and charged compounds through ion-exchange interactions, and selectivity can be obtained eliminating the first interactions with a clean-up step. The ion-exchange interactions can be anionic or cationic, and strong or weak depending on the groups present in the sorbent [1]. In this study, different zwitterionic sorbents, able to perform both anionic and cationic interactions, were synthesized and evaluated in the solid-phase extraction (SPE) of a group of contaminants. These materials are based on a silica skeleton or silica skeleton embedded with carbon microparticles[2], and functionalized with quaternary amines and sulfonic groups, so that they can establish strong anionic and cationic interactions. The pollutants selected were thirteen drugs, containing basic and acid drugs. The SPE method was optimized for each material by using LC and diode array detection. Once the SPE protocol was optimized, the best material was selected and evaluated with real samples using LC-MS/MS. Finally, the SPE/LC-MS/MS method was validated and applied to determine these drugs in river and wastewater samples.

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EXTRACTION OF CONCANAVALIN A FROM FOOD USING APTAMER-BASED AFFINITY MAGNETIC BEADS

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In recent years, food allergies have increased affecting up to 30% of the population. Allergens can produce different reactions in the human body such as digestive disorders, skin irritation or anaphylactic shock [1]. For this reason, it is necessary to develop new methods to analyze and characterize allergens in food matrices. Within allergenic groups, proteins integrate one of the most important ones including egg proteins (ovalbumin), lectins (concanavalin A, Con A) or those present in wheat (glutenins and gliadins). In particular, Con A has been one of the most studied lectins due to its numerous biological effects associated with its carbohydrate-binding properties. Lectins are typically detected by hemadsorption, hemagglutination, or bacterial agglutination assays. These tests are qualitative and determine all lectins; however, they are not efficient in discriminating between the different types of lectins. The detection of Con A is also possible using ELISA (enzyme-linked immunosorbent assay) and immunoelectrophoretic assays. Nevertheless, these tests are expensive since the use of antibodies are needed. In this sense, aptamers are interesting alternatives. These molecules are synthetic oligonucleotides that exhibit high affinity and specificity for target analytes, a moderately low-cost and easy preparation. Indeed, aptamers have been used for separation, purification, or preconcentration purposes in analytical chemistry field [2,3]. In this work, an aptamer-modified sorbent based on magnetic beads (MBs) has been developed to be used as magnetic phase to extract Con A (labeled with fluorescein isothiocyanate) by means of magnetic solid-phase extraction. Hence, the optimization of the aptamer immobilization protocol on the magnetic beads was carried out modifying the aptamer/MBs mass ratio and the immobilization time. The different materials were used for the retention of Con A in aqueous samples. The amount of aptamer immobilized on the MBs and the concentration of Con A retained by the different sorbents were evaluated by fluorescence. The developed aptamer-affinity MBs gave satisfactory recovery and repeatability.

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CHARACTERIZATION OF HONEYS FROM DIFFERENT FLORAL VARIETY BY MEANS OF ANTIOXIDANT CAPACITY AND POLYPHENOL CONTENT

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Honey is a natural food which has been used for many years. It is produced by bees from flower nectar or secretions from the living part of the plant. Therefore, honey can be multifloral when the flower nectar is not selected or uni-floral when the honey is produced basically from one flower type. This sweet food is composed by carbohydrates and water, as well as amino acids, vitamins, minerals, enzymes, organic acids and phenolic compounds [1]. The composition of honey provides it with good organoleptic and therapeutic characteristics, also providing a high antioxidant capacity, antimicrobial and anti-inflammatory activity [2]. Antioxidant capacity, which measures the nutritional value of honey, can differ depending on floral and geographical origin [3]. The main components that influence the antioxidant capacity are flavonoids, glucose oxidase, catalase, ascorbic acid, proteins, carotenoids and principally phenolic acids [4]. These compounds play an important role in human health. Currently, different methods have been described in literature to determine the total polyphenol content (such as Folin Ciocalteau method) and antioxidant capacity including the 1,1-diphenyl-2-picrylhydrazyl (DPPH) method; 2,2’azino-bis-(3-ethyl- benzothiazoline-6-sulfonic acid) diammonium salt ($ABTS^+$) assay and ferric reducing antioxidant power (FRAP) method. However, these methods are focus on the total fraction of polyphenols and do not provide a qualitative and quantitative information of the individual polyphenols that contribute to the antioxidant capacity of honey. In this sense, it is possible to determine individual phenolic compounds by high performance liquid chromatography (HPLC). In this work, honeys from different varieties (chestnut, heather and thyme), obtained at different geographical areas, have been used to determine total polyphenol content (Folin Ciocalteau method) and antioxidant capacity (FRAP, $ABTS^+$ and DPPH methods). The same samples were also analyzed by HPLC in order to determine the individual composition of phenolic compounds. Finally, both traditional assays and HPLC data were used to construct a linear discriminant analysis able to classify honeys according their floral variety.

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NEW SENSOR BASED ON POLYMER INCLUSION MEMBRANES FOR FREE COPPER AND ZINC DETERMINATION

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The development of analytical techniques for the measurement of free metal species is of paramount importance for predicting metal bioavailability and toxicity. Functionalized liquid membranes, containing a selective extractant or carrier, have been studied for this purpose and several investigations have been performed using permeation liquid membranes (PLMs)[1]. Recently, our group has been involved in the design and characterization of a new type of functionalized membranes, called polymer inclusion membranes (PIMs), for Zn speciation in hydroponic media[2] and to mimic Zn accumulation in biofilm[3]. The required technology to use this type of membrane is fairly simple and could be easily suited to a wide range of applications. In general, PIMs appear as transparent and stable films that possess good mechanical properties.

In this work, new studies are presented for Cu and Zn speciation using a PIM made of cellulose triacetate (CTA, 50% w/w) as the base polymer, di-(2-ethylhexyl) phosphoric acid (D2EHPA, 40% w/w) as the extractant, and nitrophenyl octyl ether (NPOE, 10% w/w) as the plasticizer. The sensor device incorporates the PIM interfaced between the feed phase (target water sample) and a receiving solution (0.01 M HNO_3) where the metals under study accumulated.

In order to demonstrate the applicability of this system in aqueous samples, the influence of copper and zinc concentration on the metal accumulated in the receiving solution has been evaluated in a water sample containing the two metals separately or in competitive experiments. It has been demonstrated that this sensor has a greater ability to accumulate copper than zinc and that the metal accumulated correlates with the total concentration in absence of ligands. The presence of organic ligands, such as ethylenediaminetetraacetic acid (EDTA) or humic acid (HA) significantly influences the extraction of the metals because of the formation of metal complexes. These results were compared with visual-MINTEQ calculations and a good agreement was found between metal accumulated and the percentage of free metal (non complexed metal) in the feed solution.

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COMPARISON OF DIFFERENT MEMBRANE CONFIGURATIONS IN POLAR ORGANIC CHEMICAL INTEGRATIVE SAMPLERS: INFLUENCE ON THE SAMPLING RATE OF EMERGING CONTAMINANTS

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POCIS samplers are amongst the most frequently used passive devices in environmental monitoring of organic contaminants [1]. While some work has been conducted on studying innovative sorption materials to replace the standard Oasis HLB sorbent to improve sampling rates, fewer studies have looked at innovative membrane materials [2]. Nevertheless, the membrane used to hold the stationary phase inside the sampler, strongly influences the analytes equilibrium between the sorbent phase and the water [3, 4]. In addition, the traditional polyethersulfone microporous membranes are fragile, and can easily tear during deployment and handling. More resistant membrane materials could be useful to avoid this issue. In this study, different membranes were used during in-lab calibration to determine sampling rates of a range of emerging contaminants, including acidic drugs, UV filters and estrogens. The variables studied were polymer material and pore size, which are likely to affect the kinetics and thermodynamics involved in contaminants uptake into the POCIS. Two different polymers were tested: polyethersulfone (including the standard 0.1 µm pore size as a reference membrane) and less fragile polyester membranes (including 2 different types of weaving) resulting in 4 different combinations.

Two POCIS of each type were assembled in the lab and placed in 4 beakers during a 1-week static/stirred exposure. The beakers contained 4.5 L of tap water spiked at a concentration of 2 µg L^{-1} of each analyte. At the end of the experiment, both sorbent and membranes were extracted separately, and the analysis was carried out by HPLC-MS/MS.

The results revealed a significant positive influence of the pore size on the sampling rates of some polar compounds. In addition, several hydrophobic compounds which may not be sampled with the standard POCIS were substantially accumulated in the sorbent when using the larger pore size. The effect of changing polymer material was less important or not noticeable for more polar compounds, but also allowed promising uptake of more hydrophobic compounds onto the sorbent.

This study showed the importance of membrane selection for the use of POCIS for a wider range of applications. Deeper investigation is necessary to thoroughly understand the influence of the membrane on the absorption mechanisms of contaminants onto this type of passive samplers.

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ELECTROMEMBRANE EXTRACTION OF PEPTIDES USING DEEP EUTECTIC SOLVENTS AS LIQUID MEMBRANE

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For the first time, we report electromembrane extraction (EME) of peptides using deep eutectic solvent (DES) as supported liquid membrane (SLM). DES were mixtures of coumarin, camphor, DL-menthol and thymol. Sixteen model peptides were extracted from 100 µL 50 mM phosphate buffer solution (pH 3.0), through the SLM, and into 100 µL acceptor solution consisting of 50 mM phosphoric acid (pH 1.8). EME was performed in 96-well format with 30 V to facilitate extraction of positively charged peptides. The model peptides comprised three to 13 amino acids, and differed significantly in terms of acid/base functionalities and polarity. We found pure DES to be inefficient for EME of peptides. However, with addition of a small amount of the ionic carrier di(2-ethylhexyl) phosphate (DEHP) to the DES, the extraction efficiency increased due to ionic interactions. With the most efficient SLM; coumarin and thymol mixed in molar ratio (1:2) with 2.0 % (v/v) DEHP, average recovery after 15 minutes was 55 %; five peptides were extracted with recovery > 80 %, nine peptides with recoveries in the range 40-80 %, and two peptides were not extracted (recovery < 5 %). When extraction time was extended to 45 minutes, average extraction recovery increased to 83 %. Extraction recoveries with DES were higher than previously reported in the literature for the same model peptides.

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IMMERSE GAS-DIFUSSION MICROEXTRACTION FOR SIMULTANEOUS DETERMINATION OF FIVE DICARBONYL COMPOUNDS IN INFANT FORMULA BY HPLC-PDA

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Infant formula is the only food product that may be supplied to children in the first stage of life when breastfeeding is not possible for any biological or social circumstances, thus these products must be both innocuous and chemical safe [1]. During infant formula production and storage many reactions may occur that affect organoleptic properties and decrease their nutritional value.

Maillard reaction and lipid peroxidation led to the formation of toxic dicarbonyl compounds such as malondialdehyde (MDA), glyoxal (GO), methylglyoxal (MGO), dimethyl glyoxal (DMGO), and acrolein (ARCL) which has been classified by the International agency of research in cancer (categories 2A, and 3) and suspected to be harmful to human health [2].

A new immerse gas-diffusion microextraction (GDME) approach has been successfully developed for the simultaneous analysis of MDA, ACRL, GO, MGO, and DMGO in infant formula by HPLC-PDA. The analytical features have been assessed by Food and Drug Administration (FDA) guidelines of analytical method validation [3].

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STUDY OF TOXIC COMPOUNDS IN SYNTHETIC FOOTBALL FIELDS FROM SEVENTEEN COUNTRIES: A GLOBAL PROBLEM

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Synthetic turf football field are fill of recycled tire rubber, representing a risk to human and environmental health due to its content in toxic substances which can be spread into the environment [1,2]. Therefore, this research assesses the presence of forty-two organic compounds including polycyclic aromatic hydrocarbons, plasticizers, antioxidants and vulcanisation additives in tire rubber collected in synthetic turf football fields from all the world. These substances were selected according to previous studies on synthetic turf football fields and children´s playgrounds, among other surfaces [1]. Extraction of the target compounds was performed by ultrasound assisted extraction prior to an analysis carried out by gas chromatography coupled to tandem mass spectrometry. Samples from seventeen countries (from different continents) were analyzed. Results confirmed the presence of a large number of toxic substances in the analyzed samples from the seventeen countries.

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SIMULTANEOUS ANALYSIS OF FRANGANCE ALLERGENS, SYNTHETIC MUSKS, PRESERVATIVES AND PLASTICIZERS IN HYDROALCOHOLIC GELS BY SOLID-PHASE MICROEXTRACTION

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Nowadays, hand sanitizers have become a common alternative to handwashing instead of soap and water and as a prevention measure of the spread of the COVID-19 virus [1,2]. Hydroalcoholic gels, alcohol-based hand sanitizers, can contain a whole host of chemicals including organic compounds which can be allergen substances or endocrine disruptors. For this reason, the main goal of this work is the development of a method based on solid-phase microextraction followed by gas chromatography coupled to tandem mass spectrometry (SPME-GC-MS/MS) for the simultaneous determination of a very high number of organic compounds including fragrance allergens, preservatives, plasticizers and synthetic musks. First, different preliminary studies were carried out (type of extraction, dilution, etc). The most critical experimental parameters affecting SPME (i.e. fibre coating, extraction mode, temperature) were optimized by means of an experimental design methodology. Under optimum conditions the SPME-GC-MS/MS method was successfully validated, showing good linearity, precision (repeatability, reproducibility) and quantitative recoveries at two different concentration levels. Finally, the method was applied to different hydroalcoholic gels, demonstrating the presence of toxic substances in these commercial daily care products.

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A SAMPLE PREPARATION METHOD BASED ON IONIC MATRICES FOR THE IMPROVED ANALYSIS OF microRNA BIOMARKERS BY MATRIX-ASSISTED LASER DESORPTION/IONIZATION MASS SPECTROMETRY

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MicroRNAs (miRNAs) are small non-coding RNAs of 19-23 nucleotides in length involved in gene regulation [1]. They control gene expression and their deregulation has been related to the occurrence and progression of different diseases, especially cancer [1,2]. In this study it is described the use of ionic matrices (IMs) as an alternative to conventional matrices to analyze microRNAs (miRNAs) by matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) [3]. 2, 4, 6-Trihydroxyacetophenone (THAP), 6-aza-2-thiothymine (ATT) and 3-hydroxypicolinic acid (3-HPA) and their IMs with pyridine (PYR) and butylamine (BA) are studied to analyze a standard mixture of miRNAs: miR-21, let-7g and iso-miR-16. Among all the studied matrices, ATT-PYR at 75 mg/mL in acetonitrile (MeCN):H_2O (50:50, v/v) with ammonium citrate dibasic as signal enhancer is selected as the optimal. These conditions provide the best sensitivity, with limit of detection (LOD) up to 5 nM (equivalent to 1 fmol in the spot) and excellent spot-to-spot repeatability due to the improved homogeneity of the spots compared to the conventional matrices. The applicability of the established method to direct, multiplex and untargeted analysis of miRNAs in serum samples is also investigated.

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MICROEXTRACTION OF BETA-CAROTENE, LYCOPENE AND LUTEIN FROM CARROT PEELS WASTE USING SUPRAMOLECULAR SOLVENTS

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Carotenoids are bioactive compounds of high-add value because of their beneficial effects on human health. They are precursors of vitamin A and prevent chronic and degenerative diseases thanks to their antioxidant properties. Currently, natural carotenoids are generally extracted from carrots by using large volumes of organic solvents such as hexane and acetone, which are environmentally harmful [1,2]. Furthermore, these processes are tedious, time-consuming and expensive. This study aims to develop an analytical methodology simple and in line with the green chemistry principles to perform the extraction of beta-carotene, lycopene and lutein from carrot peel waste. For this purpose, we have developed an analytical method based on the simultaneous microextraction of the three carotenoids with supramolecular solvents (SUPRAS), prior to their detection by liquid chromatography-diode array. SUPRAS are nanostructured liquid produced from colloidal solutions of amphiphiles by spontaneous processes of self-assembly and coacervation. One of the most important properties of SUPRAS is the high number of binding sites that they offer to solutes, allowing the compounds to be efficiently extracted with a low SUPRAS volume. The extraction was carried out by adding 0.4 mL of SUPRAS to 0.2 g of sample and vortex-shaking at room temperature. Then, the mixture was centrifugated to separate the SUPRAS extract. As a result, the analytical method showed a high extraction ability, with recoveries ranged 98-115%. The proposed extraction is efficient and not polluting due to the low volume of organic solvents used in line, which is in line with the principles of green chemistry. This analytical methodology is an advantageous strategy for the agro-industrial waste recovery against the existing analytical methods for the extraction of beta-carotene, lycopene and lutein.

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DETERMINATION OF NICOTINE IN ELECTRONIC CIGARETTES LIQUIDS (E-LIQUIDS) BY LARGE VOLUME INJECTION-GAS CHROMATOGRAPHY-FLAME IONIZATION DETECTION USING THE THROUGH OVEN TRANSFER ADSORPTION DESORPTION (TOTAD) INTERFACE

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E-cigarettes (ECs) are generally composed of a battery that heats an atomizer, which aerosolizes the electronic cigarette liquid (e-liquid) that contains a small amount of nicotine and flavorings dissolved in a large quantity of viscous solvents (humectants) such as propylene glycol (PG) or glycerol (GLY) [1]. The nicotine contents determination usually is performed by liquid chromatography (LC) which generally has an acceptable sensitivity but requires a manual and tedious preparation of buffer solutions which turns out to be long time and not always reproducible [2-3]. Villen´s group developed an interface named TOTAD (Through Oven Transfer Adsorption Desorption) which permits large volume injection in gas chromatography (LVI-GC) [4]. Although several methods have also been developed to analyses nicotine in e-liquids, just a few methods using gas chromatography-flame ionization detection (GC-FID) have been realized because low sensitivity of detection and difficulties related to viscous humectants [5]. In this work, a quick method for the analysis of nicotine in e-liquids by LVI-GC using the TOTAD interface has been successfully developed. The method is fully automated and presents a good repeatability (RSD for retention time below 0.022 % and for absolute peak areas below 6.626 %) and linearity (from 5 mg/L to 90 mg/L ($R_2 > 0.999$)) and sensitivity (LOD 2,572 mg/L).

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A MINIATURISED PLATFORM BASED ON MICROFLUIDICS COUPLED TO DRIED BLOOD SPOT (DBS) FOR THERAPEUTIC DRUG MONITORING

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In the framework of bioanalysis, miniaturisation of analytical procedures is an ambitious and desirable goal from the point of view of sustainability, protocol streamlining, analytical throughput and automation. To this purpose, an advanced whole blood microsampling approach based on an innovative microfluidic platform was proposed, able to collect a minute and accurate volume of only 10 µL of sample to be subjected to instrumental analysis, collected in a minimally invasive way by means of a finger prick. This technological advancement integrates in a single device a microfluidic chip with four microcapillaries and a cellulosic card for dried blood spot (DBS) sampling. Among the advantages of dried microsampling, this strategy allows to store and transport the samples at room temperature, ensuring stability profiles comparable to those of cryopreserved biological fluids [1]. Thanks to these advantages, the novel DBS-based platform developed within this research represents also a useful patient-friendly tool for home- and self- sampling, as a promising approach for therapeutic drug monitoring (TDM) of patients in order to decrease side effects and hospitalisations, with the perspective of therapy personalisation. As a proof of concept, an original bioanalytical methodology was designed and tailored for the monitoring of patients under therapy with clotiapine, a classical neuroleptic drug, chosen as test compound and analytical target. A feasible and high-throughput pretreatment protocol coupled to an original HPLC-MS method was developed in order to obtain a streamlined, yet reliable and effective analytical workflow. The optimised methodology was validated with satisfactory and promising results in terms of sensitivity and precision, for this reason it was successfully applied to real samples for TDM purposes. To demonstrate the reliability of the developed microsampling approach, the obtained results were compared with those from a reference routine plasma procedure, showing very good agreement between the two datasets. Based on these results, the developed methodology proved to be a promising bioanalytical tool to be applied in the framework of TDM, potentially paving the way to more frequent, accurate and reliable monitoring of patients under pharmacological therapies.

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CAPILLARY VOLUMETRIC BLOOD MICROSAMPLING FOR THE MONITORING OF METHADONE MAINTENANCE TREATMENT

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Opioid addiction is one of the most harmful ones and the most widespread among the population after cannabis. Illicit use of heroin and other opioids causes serious healthcare problems among the population such as overdoses, hospitalizations and deaths every year [1]. The fight and prevention against opioid addiction is very complex for the authorities and for healthcare workers. When prevention or psychological support alone are not sufficient to stem the phenomenon and to reintegrate drug addicts back into society, pharmacological cessation approaches are usually envisaged. One of the main therapies is Methadone Maintenance Treatment (MMT), in which patients are treated with methadone (MTD), a synthetic opioid also often diverted as drug of abuse on the illicit market. For this reason, it is important to monitor MTD-maintained subjects with a dual purpose: both to reduce the incidence of side effects during MMT therapy, adjust dose regimens and enhance efficacy and also to prevent possible misuse and drug diversion. An innovative and original capillary volumetric blood microsampling strategy [2] was developed for the monitoring of patients undergoing MMT. In particular, haematic microsampling granted several advantages in terms of sample stability, logistical savings and patient compliance. Furthermore, this miniaturised technology was able to simultaneously generate four sample replicates and designed to prevent sample manipulation. After analyte extraction by means of an optimised pretreatment procedure, MTD was quantified by an original HPLC-ED (coulometric detector) method, featuring high selectivity and sensitivity. The method was validated with satisfactory results in terms of extraction yield (> 90%), sensitivity (LOQ = 5.0 ng/mL) and precision (RSD% < 10.0). This analytical strategy showed to be suitable to assess MTD in blood microsamples and a promising tool in the forensic and clinical field, in order to monitor MTD levels and prevent misuse and side effect in MMT therapy.

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CHEMICAL COMPOSITION AND ANTIOXIDANT ACTIVITY OF ESSENTIAL OILS FROM *Piper marginatum* AND *Varronia curassavica*

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Oxidative stress is a state generated by an excessive increase in reactive oxygen species (ROS) and reactive nitrogen species (RNS) in an organism, which exceeds its defense capacity. Some essential oils may possess antioxidant activity making them attractive for use in cosmetic products. The main objective of this research was to study the chemical composition and to evaluate the antioxidant activity of essential oils from the aromatic plants *Piper marginatum* (Piperaceae) and *Varronia curassavica* (Boraginaceae) grown in the state of Santander (Colombia). Essential oils were obtained by microwave-assisted hydrodistillation during 1 h, using a domestic microwave oven and a Dean-Stark trap. Chemical characterization of essential oils was performed by GC/MS and their quantification by GC/FID. Antioxidant activity of essential oils was evaluated by $ABTS^{+\cdot}$ and β-carotene bleaching assays. Essential oil yields for *P. marginatum* and *V. curassavica* were 0,1% and 0,2%, respectively. Monoterpene hidrocarbons and sesquiterpene hidrocarbons were the main compounds in *P. marginatum* and *V. curassavica* essential oils. These results were different from those found in the literature [1,2]. Antioxidant activity varied between 210 and 380 µmol Trolox® for the $ABTS^{+\cdot}$ method and 3-21 µmol Trolox® for the β-carotene bleaching assay. The antioxidant activities of the essential oils examined were lower than those of the reference substances BHT and α-tocopherol, those were 6300 and 2400 µmol Trolox® for the $ABTS^{+\cdot}$ method and 431 and 557 µmol Trolox® for the β-carotene method, respectively.

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FRACTIONATION OF THE ESSENTIAL OIL FROM *CYMBOPOGON NARDUS* USING SPINNING BAND DISTILLATION

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The essential oil (EO) of *Cymbopogon nardus* (Poaceae) is commonly used in the production of mosquito repellents and perfumes [1]. In order to add value to the bioactive components of the essential oil, techniques such as fractional rotary band distillation have been developed to allow the concentration and separation of the major compounds. In this process, the essential oil of *C. nardus* obtained by steam distillation was fractioned with a B/R Instrument Spinning Band Distillation Model 800. The essential oil and fractions were characterized by gas chromatography coupled to mass spectrometry (GC/MS) and quantified by gas chromatography with flame-ionization detection (GC/FID). The major components identified in the oil were geraniol (23.8%), citronellol (18.4%) and citronellal (15%). The rectification of the essential oil produced three fractions F1, F2 and FF collected at different temperatures as follows: F1 (64 °C), F2 (77.3 °C) and FF (131.4 °C). F1 and F2 were enriched with monoterpenic hydrocarbons such as limonene (23.1 mg/g EO) and oxygenated monoterpenes such as citronellal (698 mg/g EO), while FF was mainly enriched with geraniol (259 mg/g EO) and citronellol (174 mg/g EO).

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EXTRACTION OF VOLATILE SECONDARY METABOLITES BY DIFFERENT METHODS FROM *Varronia curassavica* Jacq. AND THEIR GC/FID AND GC/MS ANALYSIS

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Varronia curassavica Jacq. (Boraginaceae) known as "*erva-baleeira*" or "*mulato*" is an aromatic shrub from the Neotropical Region, used in folk medicine to treat inflammation, ulcers, arthritis, and pain [1]. The essential oil (EO) is an ingredient in the formulation of the Brazilian topical medicine Acheflan® [2]. Its anti-inflammatory, analgesic and healing properties are mainly due to the presence of (*E*)-β-caryophyllene and α-humulene in the EO isolated from the leaves [3]. The aim of this work was to determine by gas chromatography coupled to mass spectrometry (GC/MS) and gas chromatography coupled to flame ionization detector (GC/FID) the chemical composition of the volatile secondary metabolites of *V. curassavica* obtained by microwave assisted hydrodistillation (MWHD) and headspace solid-phase microextraction (HS-SPME) [4]. Compound identification was based on chromatographic (retention times and indices, standard compounds) and mass-spectral (fragmentation pattern, comparison with databases) criteria. The essential oil isolated from aerial parts of *V. curassavica* had a yield of 0.15 ± 0.04% (w/w). Sesquiterpene hydrocarbons germacrene D (21.32 ± 0.08%) and (*E*)-β-caryophyllene (18.64 ± 0.07%) were the major EO compounds, followed by α-pinene (13 ± 1%) and α-copaene (11 ± 2%). In the volatile fraction of leaves and flowers of the plant, obtained by HS-SPME, α-pinene (24 ± 1% and 10.8 ± 0.8%) and (*E*)-β-caryophyllene (23 ± 2% and 31 ± 2%) were the most abundant metabolites, respectively.

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STUDY OF THE QUALITY OF ESSENTIAL OILS ISOLATED FROM PLANTS OF THE GENUS *Cymbopogon* CULTIVATED IN SANTANDER, COLOMBIA

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Cymbopogon martinii (Poaceace), is a plant native to South Asia. *C. martini* essential oil (EO) is used as an antimicrobial, repellent, antiseptic, and diuretic [1]. *C. nardus* grows in tropical areas, is native to India and Sri Lanka, where it is used for the treatment of rheumatism and different digestive and intestinal problems [2]. *C. martini* and *C. nardus* were collected at CENIVAM. The plant material was distilled for 60 min, in four 15 min-batches using Clevenger equipment, with a Dean-Stark trap and heating by microwave radiation (Samsung, 1000 W, 2.45 GHz). The physicochemical properties of EO were evaluated according to ISO 1242, 709, 279, 280, and 592 international standards. EO analysis was performed on a gas chromatograph (Agilent Technologies 6890 Plus, Palo Alto, CA, USA), coupled to a mass selective detector (AT MSD 5973 Network) operated in full scan mode. Capillary columns were used, viz., a DB-5MS [5% -phenyl-poly (methylsiloxane), 60 mx 0.25 mx 0.25 µm] and a DB-WAX [poly- (ethylene glycol), 60 mx 0.25 mm x 0.25 µm], split injection mode (1:30), injection temperature 250 °C, injection volume 1 µL, and electron ionization at 70 eV. The identification of the compounds was carried out by comparing their mass spectra and linear retention indices with those of the databases (Wiley, NIST, Adams). The major components in *C. martinii* EO were geraniol (60-70%), geranyl acetate (11.2-11.4%) and linalool (2.5-5.2%) and in *C. nardus* EO were citronellal (34-41%), geraniol (16-24%) and citronellol (7-9%). The physicochemical properties of EO were within the acceptance ranges established in international quality standards. The quality parameters of EOs obtained met international standards ISO 4727 and ISO 3848 and 3849 for *C. martinii* and *C. nardus*, respectively.

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EXTRACTION OF *Hyptis colombiana* (LAMIACEAE) ESSENTIAL OIL AND ITS GC/MS ANALYSIS

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Hyptis colombiana (Lamiaceae family) is a shrub native to the Colombian and Venezuelan Andes [1,2]. The genus *Hyptis* is traditionally used for the treatment of digestive disorders, menstrual disorders and respiratory diseases [3]. The plant was collected from experimental plots at the CENIVAM research center. The essential oil (EO) was obtained in a Clevenger-type microwave-assisted hydro-distillation (MWHD) equipment, with a Dean-Stark distillation reservoir; adapted to a conventional microwave oven (SAMSUNG model MS-1242zk, 1200 W). A round flask with plant material (*ca.* 200 g) and water (*ca.* 0.3 L), underwent 720 W radiation. The equipment was operated for 45 min (three 15-min intervals) with a standing time of two minutes. The EO was collected by decantation and anhydrous sodium sulfate was added to remove moisture. The essential oil yield was 0.09% (w/w). The EO analysis was carried out on a GC 7890 Plus gas chromatograph (Agilent Technologies, AT, Palo Alto, CA, USA) coupled to a mass selective detector AT MSD 5973 with electron ionization, at 70 eV. Capillary apolar column DB-5MS [60 m x 0.25 mm (id) x 0.25 µm] with stationary phase of 5%-phenyl-poly(dimethylsiloxane) and polar column DB-WAX [60 m x 0.25 mm (id) x 0.25 µm] with stationary phase of poly (ethylene glycol) were employed. The temperature of the GC oven was programmed from 45 °C for 5 min, then at 5 °C/min to 250 °C. The EO compound identification was based on comparison of their mass spectra with those from databases (ADAMS, NIST02, Wiley). The main compounds identified were *trans*-β-caryophyllene (33.8%), germacrene D (22.3%), and cariophyllene oxide (13.8%). It has been previously reported that these compounds may have antimicrobial activity [2].

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EXTRACTION AND CHEMICAL COMPOSITION OF SECONDARY METABOLITES FROM *Satureja viminea* (LAMIACEAE)

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Satureja viminea (Lamiaceae family) is an aromatic plant distributed in Jamaica, Cuba, Costa Rica, and Colombia [1]. *S. viminea* is used to soothe abdominal pains and is considered to have astringent and antibacterial properties [2]. The plant material was collected from experimental plots at the CENIVAM research center. Essential oil (OE) was obtained by microwave-assisted hydro-destillation (MWHD) using a Clevenger apparatus, in a conventional microwave oven (SAMSUNG model MS-1242zk, 1600 W). The analysis was performed on a GC 7890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with a mass selective detector AT MSD 5975C (with electron ionization, 70 eV). Fused-silica capillary apolar column DB-5MS [(J&W Scientific) of 60 m × 0.25 mm id, coated with 5% phenyl poly(dimethylsiloxane), 0.25 µm film thickness] and polar column DB-WAX [(J&W Scientific) of 60 m × 0.25 mm id, coated with poly(ethyleneglycol), 0.25 µm film thickness] were used. The extract was obtained by solid-liquid extraction with ethanol-water (3:1, v/v). Extract analysis was carried out using an HPLC 1200 *Infinity* (*AT,* Palo Alto, CA, USA), coupled to a diode array detector (DAD, G1315D). A Gemini column (Phenomenex, Torrance, CA, USA), of 250 mm x 4.6 mm id, x 5 µm, particle size was employed, at 25 °C. The ORAC assay was implemented in a 96-well microplate reader (Turner Biosystems Inc., Modulus Microplate Reader II). The main compounds identified by GC/MS were *p*-mentha-3-en-8-ol (21-58%), pulegone (10-16%), *trans*-β-caryophyllene (6.5-11.7%), and *cis*-pulegol (5.5-29.7%). In the extract, rosmarinic acid, kaempferol and naringenin were identified. According to the ORAC assay, *S. viminea* extract had a 6400 ± 240 µmol Trolox® value, higher than those of BHT (470 ± 13) and α-tocopherol (550 ± 13).

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EXTRACTION OF *Ambrosia peruviana* ESSENTIAL OILS FROM COLOMBIA AND THEIR CHEMICAL CHARACTERIZATION

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Ambrosia peruviana (Asteraceae), known as altamisa, is an aromatic plant native to Peru and cultivated in various Latin American countries. It is traditionally used as an antibacterial, antiparasitic, emollient, analgesic, insecticide agent, and for the treatment of infections and menstrual cramps [1,2]. The species were collected from experimental plots at the CENIVAM research center. The essential oil (EO) was obtained by hydrodistillation assisted with microwave radiation using a Clevenger equipment, with a Dean-Stark trap and a microwave oven (Samsung, 1000 W, 2.45 GHz) operated at 60% of its capacity. EO analysis was performed on a gas chromatograph (Agilent Technologies 6890 Plus, Palo Alto, CA, USA), coupled to a mass selective detector (AT MSD 5973 Network, full scan mode), split/splitless injector (split 30: 1) and a ChemStation data system, G1701-DA, which included the ADAMS, NIST and WILEY spectral libraries. Fused-silica capillary columns DB-5MS [(J&W Scientific) of 60 m x 0.25 mm id, coated with 5% phenyl poly(dimethylsiloxane), 0.25 µm flim thickness] and DB-WAX [(J&W Scientific) of 60 m x 0.25 mm id, coated with poly(ethyleneglycol), 0.25 µm flim thickness] were used. The GC oven temperature was programed from 45 °C to 150 °C (5 min) at 4 °C/min, then to 250 °C (5 min) at 10 °C/min and to 275 °C (15 min) at 10 °C/min. *ar*-Curcumene (24.6%), β-bisabolene (17.7%), γ-curcumene (13.8%), phytol (5.2%), spatulenol (4.8%), germacrene D (3.4%), and neryl acetate (3.0%) were detected as major compounds in the *A. peruviana* essential oil. This chemical composition differed from that reported for the species cultivated in Venezuela [3], however, the production and type of secondary metabolites depends on the plant growth conditions, environmental variations, soil type and the presence of different microorganisms in soils.

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Lippia origanoides (VERBENACEAE) STEAM DESTILLATION STUDY

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Due to antibiotic residues found in poultry meat and the microorganism resistance to conventional treatments, the use of the essential oil (EO) isolated from *Lippia origanoides* (Verbenaceae) as a growth-promoting additive and antimicrobial agent in poultry has emerged as an interesting alternative. The *L. origanoides* EO activity is attributed to the high content of terpene phenols, namely, thymol and carvacrol [1]. EO from *L. origanoides* dried plant material was obtained by steam distillation. Distillation was carried out in a 0.1 m^3 stainless steel still for *ca.* 4 h. To evaluate the effect of particle size, bed density and steam flow on the combined response, i.e., yield and composition of EO, an experimental 2^3 design with three replicates at the center point was applied. The EO composition was represented by the carvacrol: thymol ratio. The combined response corresponded to the sum of the normalized data multiplied by factors of 0.7 and 0.3 for EO yield and composition, respectively. The EOs were analyzed by gas chromatography coupled to mass spectrometry (GC/MS) and gas chromatography with flame ionization detector (GC/FID). The highest EO yield obtained was 0.97% and only the particle size factor had a significant effect on the combined response. The major compounds of *L. origanoides* EO were *p*-cymene (3-6%), thymol (18-25%), carvacrol (23-31%), and *trans*-β-caryophyllene (6-12%).

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EXTRACTION OF PHENOLIC COMPOUNDS FROM *Pogostemon cablin* Benth: UHPLC-ESI$^+$-ORBITRAP-MS IDENTIFICATION AND STUDY OF THEIR ANTIOXIDANT ACTIVITY

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The extract from *Pogostemon cablin* (Lamiaceae), is used in cosmetics [1,2]. *P. cablin* leaves were obtained from plants cultivated in experimental plots at the CENIVAM research center. The extract was obtained by solid-liquid extraction with ethanol-water (3:1, v/v). Extract analysis was carried out by an UHPLC Dionex^{TM} UltiMate^{TM} 3000 (Thermo Fisher Scientific, Bremen, Germany), coupled to an Orbitrap^{TM} mass detector (Exactive Plus, Thermo Fisher Scientific, Bremen, Germany), with a heated electrospray interface (HESI), operated in positive ion mode, at 350 °C. The separation was made at 30 °C in a Hypersil GOLD^{TM} aQ column (Thermo Fisher Scientific, Sunnyvale, CA, USA), of 100 mm x 2.1 mm id, x 1.9 µm, particle size. The mobile phase was as follows: A-water (formic acid, 0.2%) and B-acetonitrile (formic acid, 0.2%). The ORAC assay was implemented in a 96-well microplate reader (Turner Biosystems Inc., Modulus Microplate Reader II). Apigenin-diglycoside, apigethrin, apigenin, pachipodol, 3,5-dihydroxy-7,4'-dimethoxyflavone, 5-hydroxy-7,4'-dimethoxyflavanone, and retusin were identified by LC-MS using the exact masses of the protonated target compounds, isotopic ratios, elemental compositions, fragmentation patterns [3], and using certified standards. According to the ORAC assay, *P. cablin* extract had a 640 ± 9 µmol Trolox$^{®}$ value, higher than those of BHT (460 ± 9) and α-tocopherol (550 ± 13). *P. cablin* extract contained mainly phenolic compounds of the flavone-type and its oxygen-radical absorption capacity was similar to that exhibited by commercial antioxidants, BHT and α-tocopherol.

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EXTRACTION OF SECONDARY METABOLITES FROM *Salvia aratocensis* AND THEIR GC-MS AND LC-MS ANALYSIS

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Salvia aratocensis belongs to the Lamiaceae family, it grows in the Eastern Cordillera in the departments of Santander and Boyacá in Colombia [1]. The plant material was collected from an experimental plots at the CENIVAM research center. The essential oil was obtained by a Clevenger-type microwave-assisted distillation (MWHD), in the apparatus with Dean-Stark trap. The analysis was performed on a GC 7890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with a mass selective detector AT 5975C (with electron ionization, 70 eV). A fused-silica capillary apolar DB-5MS column [(J&W Scientific) of 60 m × 0.25 mm id, coated with 5% phenyl poly(dimethylsiloxane), 0.25 µm film thickness] and polar DB-WAX column [(J&W Scientific) of 60 m × 0.25 mm id, coated with poly(ethyleneglycol), 0.25 µm film thickness] were used. The extract was obtained by solid-liquid extraction with ethanol-water (3:1, v/v). Extract analysis was carried out using an UHPLC Dionex^{TM} UltiMate^{TM} 3000 (Thermo Fisher Scientific, Bremen, Germany), coupled to an Orbitrap^{TM} mass detector (Exactive Plus, TFS, Bremen, Germany), and a heated electrospray interface (HESI), operated in positive ion mode, at 350 °C. The separation was made at 30 °C in a Hypersil GOLD^{TM} aQ column (TFS, Sunnyvale, CA, USA), of 100 mm x 2.1 mm id, x 1.9 µm, particle size. The ORAC assay was implemented in a 96-well microplate reader (Turner Biosystems Inc., Modulus Microplate Reader II). *trans*-β-Caryophyllene (20%) was the major component of the *S. aratocensis* essential oil, followed by α-humulene (10%), germacrene D (33%), α-cadinene (8%), and *trans*-calamenene (8%). In the hydroethanolic extract, the phenolic major compounds, salvigenin, genistein and cirsimaritin were identified. According to the ORAC assay, *S. aratocensis* extract had an 890 ± 38 µmol Trolox$^{®}$ value, higher than those of BHT (460 ± 9) and α-tocopherol (550 ± 13).

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STUDY OF THE ESSENTIAL OIL OBTAINED FROM AERIAL PARTS OF *OCIMUM CAMPECHIANUM* CULTIVATED IN COLOMBIA.

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Ocimum campechianum, commonly known as clove basil, is a perennial and woody aromatic herb of the Lamiacea family [1]. This plant has been used as a repellent and, thanks to the potential antioxidant activity of its essential oil (EO), it has also been used in cosmetics and in the folk medicine to treat diabetes, as well as to relieve the symptoms of stomach pain, conjunctivitis and various conditions related to cellular oxidation [2-4]. In the present study, the essential oils of *O. campechianum* fresh and dry plant material were isolated and characterized by microwave-assisted hydrodistillation technique (MWHD), the yields of 0,37% and 0,38% were obtained respectively; in the same way, EO was isolated from the aerial parts such as flowers (0,25% yield) and leaves (0,63% yield). The essential oils were characterized by gas chromatography coupled to mass spectrometry (GC/MS); 31 compounds (relative GC area > 0,1%) were identified, of which eugenol (38±2,1%), 1,8-cineole (18±1,2%), (*E*)-β-caryophyllene (6,4±0,1%), β-selinene (8,8±0,6%) and germacrene D (4,3±0,2%), were the main compounds, Quantification by GC/FID showed that while eugenol content was higher in flower (426±34,3 mg substance/g EO) essential oil than in the oil from leaves (405±17,0 mg substance/g EO), the leaf oil was richer in 1,8-cineole than the flower essential oil. The high levels of eugenol in *O. campechianum* are related to its potential antioxidant activity according to the study carried out by Adefegha *et al.* [3], where eugenol was shown to have a significantly higher antioxidant capacity (2,58 µmol TEAC/g) than BHT (1,84 µmol TEAC/g) and BHA (1.68 µmol. TEAC/g). Therefore, the high eugenol content in *O. campechianum* EO represents an attractive opportunity for the development of bioproducts for the agricultural, cosmetic, pharmaceutical, and biomedical sectors [4].

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ISOLATION OF *Turnera pumilea, Achyrocline satureioides AND Chromolaena moritziana EXTRACTS AND STUDY OF THEIR* ANTIOXIDANT AND PHOTOPROTECTIVE ACTIVITIES

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There is a growing interest on the incorporation of natural ingredients that could improve the sunscreen product properties because some phenolic compounds present in plants play an important role as photoprotectors. The aim of the present study was to obtain hydroalcoholic extracts from post-distilled plant material (stems and leaves) of *Turnera pumilea* L., *Achyrocline satureioides* (Lam.) DC., and *Chromolaena moritziana* (Sch. Bip.) R.M. King & H.Rob. and to evaluate their *in vitro* antioxidant and photoprotective activities. Extracts were obtained by ultrasound-assisted solvent extraction method. The extraction conditions were follows: 70% aqueous ethanol; solvent: sample ratio 20:1 (v/w); extraction temperature 50 °C; and extraction time 60 min. The antioxidant activity of the extracts was assessed by two different *in vitro* tests: the β-carotene-linoleic acid bleaching assay and the oxygen-radical absorbance capacity (ORAC) assay. These results were compared with references substances butylated hydroxytoluene (BHT) and α-tocopherol. *In vitro* photoprotection efficacy was evaluated according to the following parameters: estimated sun protection factor (SPF) and critical wavelength (λ_c). The photoprotective effect was evaluated by the spectrophotometric method, which measured the UV absorption of each sample followed by the application of the Mansur equation to obtain the final SPF. The antioxidant activity expressed in µmol Trolox®/ g extract, varied between 24,3 and 27,1 for β-carotene-linoleic acid bleaching assay and 930 and 1690 for ORAC assay. *C.moritziana* extract (CME) presented the highest antioxidant activity (27 ± 0,15 µmol Trolox®/ g extract) for β-carotene-linoleic acid bleaching assay and for ORAC (1690 ± 97 µmol Trolox®/ g extract). The SPF of the extracts varied between 16,6 and 17,40, and the obtained UV absorption profile allowed to classify *T. pumilia* and *C. moritziana* extracts as broad spectrum ($\lambda_c \geq 370$ nm). CME also presented the medium sun protection factor SPF (17,40 ± 0,07) and λ_c from 371 to 372 nm. According to these results, the three extracts evaluated in this research could be considered as a potential source of natural ingredients with UV-absorption and antioxidant capacities.

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FRACTIONATION AND CHEMICAL CHARACTERIZATION OF PLANT EXTRACTS OBTAINED BY SFE FROM RESIDUAL BIOMASS OF PROMISING AROMATIC AND MEDICINAL SPECIES

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Aromatic species are destilled to obtain their essential oil; however, frequently the extraction yields are close to or less than 1% by weight. Therefore, a large amount of plant material is discarded or used mainly for composting [1]. New knowledge and technologies may allow to promote the use and transformation of this raw material with low economic value into value-added products. Colombia is located in a favorable geographical region, it is the second most biodiverse country in the world, a quality that has not been fully exploited, where plant species that could present properties of interest are underused or unknown [2]. Species present in Colombian biodiversity such as *Varronia curassavica*, *Turnera diffusa* and *Lippia origanoides*, are considered promising. Previous studies have confirmed the presence of flavonoids, compounds that have bioactive properties such as antioxidant [3], cytotoxic [4], antimicrobial [5], or other activities. Various authors affirm that the study of plant species is important due to the development of new formulations that are specific in their pharmacological action[6], and they realize the importance of separating complex samples into their individual constituents in order to identify the compounds that contribute the greatest biological potential [7]. For this reason, preparative liquid chromatography (Prep-HPLC) was used in this study. This technique allows the fractionation of extracts and the subsequent collection of their individual constituents in high purity [8]. Residual biomass of *T. diffusa, L. origanoides* and *V. curassavica* generated by the distillation process, were used as a substrate to obtain extracts using supercritical fluid extraction (SFE). Extraction yields of 1.20%, 1.75% and 1.88% were obtained, respectively. The chemical characterization of the extracts was carried out using instrumental techniques of chemical analysis such as high efficiency liquid chromatography (HPLC/DAD) and ultra-high efficiency liquid chromatography coupled to *Orbitrap* mass spectrometry (UHPLC/*Orbitrap*-MS).

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OPTIMIZATION OF THE OPERATIONAL CONDITIONS OF AN ULTRAFILTRATION TUBE-IN-TUBE MEMBRANE REACTOR FOR THE REMOVAL OF CECS IN URBAN WASTEWATERS

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Several governments across the globe are investing in upgrading urban wastewater treatment plants with advanced treatment technologies, regarding the removal of contaminants of emerging concern (CECs) which can pose a risk both for the ecosystem and environmental health. Antibiotics are pharmaceuticals of great interest which irrational use and high presence in water is causing microbial resistance. The use of Advanced Oxidation Processes (AOPs) offers a good option for tertiary treatment in urban wastewaters treatment plants [1] to remove these CECs. In this work, a new conceptualized device based on an outer quartz tube and an inner tubular ceramic ultrafiltration membrane is proposed as a photoreactor that operates in continuous mode for the removal of fourteen antibiotics in urban wastewater (UWW). By testing different oxidants such as H_2O_2, $S_2O_8^{2-}$ and O_3, being activated through the action of UVC light, this photoreactor was assessed for the removal of the target antibiotics. To achieve the optimum operational conditions, several parameters were studied, such as the pH and flow rate of the water, the oxidant dose and the requirement of UVC lamps or photocatalyst support. The ozonation showed to be the most efficient process, resulting in more than 95% removal of 12 out of the 14 target antibiotics in UWW, followed by Ag_2MoO_4/UVC/$S_2O_8^{2-}$ system (5 antibiotics removed > 60% in UWW). Finally, the presence and identification of transformation products was conducted by ultra-high performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry.

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INNOVATIVE MICROEXTRACTION TECHNIQUES FOR MONITORING VOCS EMITTED FROM TREE LEAVES UNDER EXTREME WILDFIRE CONDITIONS

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Ongoing climate changes have created more frequent drought and heatwave conditions that contribute to the occurrence of extreme fire events. As a result, the consequences of extreme wildfires in lives, nature, and infrastructures have brought importance over the understanding of the different causes behind this type of phenomena, especially when it comes to sudden changes in the fire's behavior. Studies have suggested that gases emitted from heated vegetation, such as volatile organic compounds (VOCs), can be more reactive in certain atmospheric conditions, and could even accumulate under vegetation, intensifying the fire-spread [1,2]. In the last decades, several modern sample preparation techniques have been used for monitoring VOCs released from different tree species, such as solid-phase microextraction (SPME) and more recently, bar adsorptive microextraction (BAµE). Both microextraction approaches have been also used for trace analysis of many classes of organic compounds and could be a great alternative for VOCs analysis [3]. In the present work, we proposed a comparative study of the performance of BAµE and SPME in the headspace (HS) mode, followed by gas chromatography coupled to mass spectrometry (GC-MS) analysis, to evaluate VOCs emissions from leaves of the main four Portuguese tree species (*Pinus pinaster, Eucalyptus globulus, Quercus robur, and Quercus suber)* and *Eucalyptus globulus'* essential oil, when subjected at different temperatures. The results obtained suggest that higher temperatures lead to an increase of VOCs emitted from the leaves studied. Also, preliminary data obtained from HS-BAµE assays indicate that this approach might be a great alternative for VOCs analysis in this context, as it implies easy manipulation and cost-effectiveness.

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A 3D PRINTED C18 DISC USED FOR ONLINE SOLID-PHASE EXTRACTION THROUGH A FLOW INJECTION SYSTEM COUPLED TO HPLC-DAD FOR THE DETERMINATION OF FLAVONOIDS IN CITRUS FLAVEDO

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This work presents a cheap 3D printed device that is fabricated and coated with a C_{18} extraction resin and used in an online coupling system between a flow analysis system and a high-performance liquid chromatography with photodiode array detection for the accurate and sensitive determination of six flavonoids (naringine, naringenin, hesperidin, hesperetin, diosmetin and tangeretin) in three kinds of citrus fruit external peel (flavedo). The solid phase extraction is performed automatically loading the sample and solvents to perform the extraction of the analytes and making a matrix clean-up, followed by the elution with 0.3 mL of acetonitrile. Then 10 µL is on-line injected into the chromatographic system. Up to 19 extractions can be carried out with each 3D printed device before its renewal.

Limits of detection and quantification were lower than 4.69×10^{-2} µg mL^{-1} and 1.88×10^{-1} µg mL^{-1}, respectively. The method was successfully applied to the analysis of 8 citrus flavedo samples from three different kinds of citrus fruits. The proposed method provides a fully automated system with a good precision and sensitivity, as well as minimizing solvents, sample, time and money consumptions comparing with the off-line extraction methods.

The developed procedure represents an alternative to manual processes with the advantage of a low reagent consumption and the performing of sample pre-treatment and injection unattended, resulting in a significant time saving for the analys, and reducing the analytical costs.

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EXTRACTION OF PROTEINS AND PHENOLIC COMPOUNDS USING HIGH VOLTAGE ELECTRICAL DISCHARGES (HVED) IN COMBINATION WITH DEEP EUTECTIC SOLVENTS (DES)

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High Voltage Electrical Discharges (HVED) improve the kinetics and yields in the extraction of intracellular components such as proteins and polyphenols. This green technique creates an intense electric field that generates electrical breakdowns. This phenomenon comes along with the generation of high amplitude shock waves, cavitation bubbles, and liquid turbulence, all resulting in the breakage of cell membranes and walls and in the release of intracellular biomolecules [1]. This pretreatment must be followed by a step to separate targeted compounds from other released compounds. This work proposes the extraction of proteins and phenolic compounds, after pre-treatment with HVED, using deep eutectic solvents. These solvents are sustainable, inexpensive, non-toxic, and biodegradable and they are constituted by two or more compounds acting as hydrogen bond donors or hydrogen bond acceptors [2]. The HVED parameters that were optimized to maximize the release of proteins and polyphenols from pomegranate seeds were pulse number and solid-liquid ratio. Next, released compounds were extracted at 50 ºC, with agitation, using different DES or alkaline extraction. Extraction of proteins and polyphenols without HVED pre-treatment was also carried out as control. Protein and polyphenol contents in the extracts significantly increased with the HVED pre-treatment, especially when it was followed by an alkaline extraction. Proteins and phenolic compounds were identified by HPLC-ESI-Q-TOF-MS/MS. Results demonstrated the coextration of both compounds.

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OCURRENCE OF COMMON PLASTIC ADDITIVES AND CONTAMINATS IN MUSSEL SAMPLES: VALIDATION OF ANALYTICAL METHOD BASED ON MATRIX SOLID-PHASE DISPERSION

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This work presents a new, effective and simple multiresidue analytical methodology consisting of matrix solid-phase dispersion extraction technique (MSPD) combining with high-performance liquid chromatography equipped with a diode array detector (HPLC-DAD), for the simultaneous determination of eleven endocrine-disrupting chemicals (EDCs) in mussel samples from Galician Rias (Spain). The environmental pollutants studied were bisphenols (bisphenol-A (BPA), bisphenol-F (BPF), bisphenol-S (BPS)), alkylphenols (nonylphenol-9 (NP-9) and nonylphenol (NP)), phthalates (diethyl phthalate (DEP), dibutyl phthalate (DBP) and di-2-ethylhexyl phthalate (DEHP)), as well as other persistent organic contaminants related that may be adsorbed on microplastic surface, such as organochloride pesticides (dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethane (DDD), dichlorodiphenyldichloroethylene (DDE)). Parameters affecting to MSPD extraction efficiency (type of sorbent, mass sample:sorbent ratio, volume and nature of extraction solvent) were optimized. The proposed method provided satisfactory quantitative recoveries (80-100%), with RSDs lower than 7% (n= 3). The matrix-matched calibration curves in all cases were linear in the level range of 0.32–120.00 µg/Kg with quantification limits between 0.25-16.20 µg/kg. The novel developed MSPD-HPLC methodology provided good sensitivity, accuracy, and repeatability for quality controls analysis in wild raw mussel samples.

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EVALUATION OF THE SAMPLE TREATMENT INFLUENCE ON THE SUSTAINABILITY ASSESSMENT OF ANALYTICAL METHODS: HPLC AND CE

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Sample preparation is the preliminary step in many analytical techniques for the determination of the analyte(s). Among several sample treatment procedures, extraction technique is commonly employed as a sample preconcentration step to separation analytical methods such as chromatography (HPLC) [1] or capillary electrophoresis (CE) [2]. This sample preparation step is susceptible of evaluation in order to find the optimal conditions for the extractive procedure. With the aim of evaluating the influence of the sample treatment in several analytical determinations, the hexagon pictogram has been applied to quantitatively evaluate the method in terms of sustainable chemistry [3,4]. The sample treatment is included as a block within the figures of merit of the hexagon tool, that describes the adequacy of the sample treatment to sustainability aspects. Several items are considered as shown in Figure 1 and penalty points are assigned, giving rise to an overall score from 0 to 4. The lower the score, the better the adaptation of the sample treatment for providing a reliable analytical result.

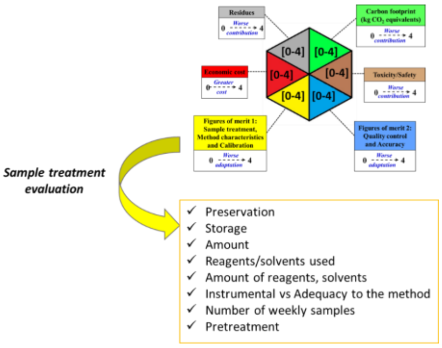

Figure 1. Hexagon pictogram including the itms for the sample treatment evaluation.

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NEW MOF-199 COATING FOR SOLID-PHASE MICROEXTRACTION OF VOLATILE ORGANIC COMPOUNDS FROM AIR

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Solid-phase microextraction (SPME) fibers based on metal organic frameworks (MOFs) might be able to address some of the shortcomings of the existing commercial SPME fibers [1]. MOFs have permanent porosity with homogeneous structured nanoscale pores, high surface area (e.g. 7000 m^2/g) [2], high mechanical and thermal stability (up to 500°C) [1] with the possibility of modification in order to improve their selectivity toward different molecules [3]. MOF-199 is a promising SPME coating demonstrating effective extraction of benzene homologues, organochlorine pesticides and polycyclic aromatic hydrocarbons [1]. In this study, the *in situ* solvothermal synthesis method was optimized for manufacturing mechanically stable 22±3 µm MOF-199 SPME coating with high surface area (1478 m^2/g). Extraction effectiveness of nine VOCs from 20-mL air samples using the developed fiber ranged between 35 and 88%; the distribution coefficients were 9.4×10^4 – 127×10^4. The developed MOF-199 SPME coating was more effective than 85-µm Carboxen/polydimethylsiloxane fiber for extraction of benzene, toluene and methylene chloride - distribution coefficients were higher by 2.3, 2.1 and 1.2 times, respectively. MOF-199 exhibited high selectivity for low molecular weight VOCs compared to 65-µm polydimethylsiloxane/divinylbenzene fiber. For MOF-199 coating, it was impossible to obtain accurate calibration plots by analyzing the standards prepared by injecting solutions of analytes in a solvent (like methanol) to air because of the negative effect of high solvent concentrations on the fiber performance. However, calibration can be obtained by analyzing VOC standards prepared using gas generating device or a serial dilution of a gas standard prepared by injecting pure analytes.

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ILLICIT DRUGS ASSESSMENT IN TAP WATER FROM FIVE EUROPEAN COUNTRIES BY SUPRAMOLECULAR SOLVENT-BASED EXTRACTION

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New research findings have proved the presence of illicit drugs in tap water from different European Union (UE) state members, presumably because of contamination of the drinking water sources (e.g. rivers, lakes, etc.) and the inefficiency of the treatments used for their removal in both wastewater treatment plants and water purification plants [1]. The main goal of this study has been to assess the exposure risk of the European population to the main groups of illicit drugs (i.e. cannabinoids, opioids, cocaine and amphetamines) through water intake. For this purpose, we have developed an analytical method based on the simultaneous microextraction of the target drugs in tap water with supramolecular solvents (SUPRAS) and their detection by liquid chromatography-tandem mass spectrometry (LC-MS/MS) in tap water. The developed method has been validated according to the European guidelines 2002/657/EC for thirteen drugs and metabolites (6-monoacetylmorphine; methadone; cocaine; codeine; benzoylecgonine; 3,4-methylenedioxyethylamphetamine; 3,4-methylenedioxymethamphetamine; 3,4- methylenedioxyamphetamine; amphetamine; methamphetamine; delta-9-tetrahydrocannabinol; cannabinol; and 11-nor-9-carboxy- delta-9-tetrahydrocannabinol). This method accomplishes both the analytical and operational features needed for tap water monitoring of drugs thanks to its high sensitivity (method quantification limits ranged 3-21 pg/mL), excellent extraction efficiency (recoveries ranged 80-120%), high reproducibility (relative standard deviation 1-18%), sustainability (SUPRAS are green solvents), simplicity and low-cost. Tap water samples (n>100) have been collected from different locations of five European countries (Portugal, Spain, France, Belgium and Germany) and were analysed under the proposed method. As an example, cocaine (0.12 ng/mL), and cocaine (0.16 ng/mL) and methamphetamine (0.95 ng/mL) were found in the tap water from Madrid (Spain) and Paris (France), respectively. This shows that current drinking water treatments are inefficient and the presence of illicit drugs in tap water needs to be monitored for ensuring tap water safety and quality for humans.

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DETERMINATION OF HYDROXYTYROSOL IN FOOD SUPPLEMENTS BY HPLC-DAD

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Hydroxytyrosol (HT) is a phenolic compound with antioxidant properties present in olive leaves and oil. Besides its antioxidant activity, HT can also improve endothelial dysfunction, lipid profiles, hemostatic profiles and has anti-inflammatory properties, among other health benefits[1]. Thus, the interest in using HT as a novel nutraceutical by the nutraceutical and food industries is rising in the last years. Indeed, the number of food supplements on the online market and pharmacies has increased since the recent EU authorization for the placing on the market of hydroxytyrosol as a novel food ingredient under Regulation (EC) No 258/97 of the European Parliament and the Council[2]. This work aimed to develop a methodology for the extraction and the determination of HT in food supplements available in the market online and in pharmacy. The extraction conditions of HT were optimized using ultrasound-assisted extraction, and a method based on high-resolution liquid chromatography with a diode detector (HPLC-DAD) was developed for the identification and quantification of the bioactive. For that, a C18 (150 x 3mm, 5µm size of the particle) column and a mobile phase consisting of water and acetonitrile acidified with 0.1% formic acid were used for the analysis. The method was validated in terms of linearity, limits of detection and quantification, repeatability, and recovery. Acceptable linearity (R^2 0.9999), adequate recovery (> 95 % in most cases), and good sensitivity (LOD 25 µg/L) were obtained. Furthermore, the presence of HT in all samples was confirmed using liquid chromatography coupled to mass spectrometry (LC-MS/MS) operated in negative ESI (Electrospray System Ionization) mode. The concentrations of HT determined in all food supplements were above the LOQ, in the range between 3.21 and 76.9 mg/g. The results showed that the methodology proposed was suitable for the determination of HT in the different types of food supplements studied, and its amounts varied significantly according to the selected product.

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ASSESSMENT OF HONEY AUTHENTICITY BY ANALYSIS OF AROMA VOLATILES USING HIGH-CAPACITY SORPTIVE EXTRACTION (HISORB) AND GAS CHROMATOGRAPHY – MASS SPECTROMETRY

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The analytical characterisation of honey has been an object of study for the last few decades driven by increasing concerns over product quality and authenticity. Volatile organic compounds (VOCs) are responsible for the aroma of this natural product, providing characteristic aromatic bouquets. The combined effect of several factors contribute to the distinct aromas; namely climate conditions, geographical location of production, flower nectar composition and post-harvest processes. The VOCs identified range widely in compound class and molecular weight, with some key distinguishing compounds being present at low levels, making the analytical process challenging and time spent data processing laborious. High-capacity sorptive extraction (HiSorb) allows a simple, solvent-free method for extraction of volatile compounds in honey. A simple HiSorb-based protocol has been developed for Gas Chromatography-Mass Spectrometry analysis of commercial honeys. Data mining and chemometrics are then performed through an intuitive software application, rapidly identifying key differences between the VOC profiles in order to distinguish between commercial, low-cost through to luxury branded, and locally-produced honeys.

DISPERSIVE SOLID-PHASE EXTRACTION USING MAGNETIC CARBON NANOTUBE COMPOSITE FOR THE DETERMINATION OF EMERGING MYCOTOXINS IN HUMAN URINE

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Dispersive magnetic solid-phase extraction (DMSPE) has received growing attention for sample treatment preconcentration due to its advantages, mainly related with the high surface area to volume ratio and the ease of application. Mycotoxins are a type of contaminants that can bioaccumulate in fluids, tissues and organs, as well as affect the nervous, endocrine and immune systems. Due to their toxicity, the European Union has established or recommended maximum permissible contents for some of these contaminants in various foods [1]. In the present work, the potential of DMSPE for the determination of emerging mycotoxins (enniatins A, A1, B and B1 and beauvericin), for which the European Food Safety Authority suggest that chronic exposure might be a concern [2], is investigated for the first time. Different magnetic nanoparticles were tested and a magnetic multiwalled carbon nanotube (Fe_3O_4@MWCNT) composite was selected for the extraction and preconcentration of the five target mycotoxins in human urine samples before their analysis by ultrahigh performance liquid chromatography coupled to high resolution mass spectrometry (UHPLC-HRMS). The nanocomposite was characterized by energy dispersive X-ray spectrometry, scanning electron microscopy, Fourier transform infrared spectrophotometry and X-ray diffraction. The different parameters affecting the adsorption and desorption of DMSPE steps were optimized and the method was fully validated. Due to a matrix effect, matrix-matched calibration method was applied for samples quantification. In this way, limits of quantification of between 0.04 and 0.1 µg/L, RSD values lower than 12% and recoveries between 89.3 and 98.9% were obtained, depending on the mycotoxin. Finally, a study of the reuse of the Fe_3O_4@MWCNT composite was carried out, confirming that it can be reused at least four times.

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HEADSPACE EXTRACTION COUPLED WITH GC-IMS FOR DETECTION OF ADULTERATED HONEY BASED ON UNTARGETED ANALYSIS

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Honey is a highly valued food for its nutritional benefits and excellent properties. Its high demand and relatively high price have made it a frequent target for adulteration. Currently, it is considered one of the six most adulterated foods in the world [1]. In this work, headspace gas chromatography coupled to ion mobility spectrometry (HS-GC-IMS) is proposed for the detection of adulterated honey and its classification according to the percentage of adulteration by sugar cane or corn syrup. The proposed method consists of the injection in splitless mode of 750 µL of the headspace into the GC-IMS, after incubation of 1 g of honey at 100 °C for 15 min. The fingerprint of the sample is obtained without sample pre-treatment and takes only 32 min of analysis. Headspace sampling allows the extraction of volatile compounds inside the vial and therefore, avoids the accumulation of non-volatile residues in the GC-IMS system. In order to develop this methodology, a total of 198 honey samples were analyzed: 56 pure honeys from different botanical origins and 142 adulterated honeys (71 with sugar cane and 71 with corn syrup). The GC-IMS coupling combines the good selectivity of GC with the high sensitivity of IMS, providing a three-dimensional topographic map. After an exhaustive data treatment, three different OPLS-DA models were constructed using the 80% of the samples, and the remaining 20% was used for method validation. The differentiation between pure and adulterated honey had a validation success of 97.4%, and the assessment of adulterant content was obtained with a 93.8% validation success rate for both adulterant agents assayed. Finally, to check the applicability of the method, nine samples of commercial honey were analyzed by the proposed methodology and seven of them were classified as honey adulterated with corn syrup. The good results achieved evidence the effectiveness of the proposed method, since it is a rapid and easy methodology using only headspace for the extraction of volatile compounds.

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MULTI-RESIDUE DETERMINATION OF EMERGING POLLUTANTS IN MUSSEL (MYTILUS GALLOPROVINCIALIS)

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Multi-residue methods are intended to show the whole picture of the organic pollutants present in the samples employing a single extraction procedure, hence saving resources and time. In the present study, 44 multi-residue procedures combining different QuEChERS and clean-ups were compared for the extraction of 10 pharmaceuticals, 5 pesticides, 5 perfluoroalkyl substances and 2 illicit drugs in mussel (*Mytilus galloprovincialis*). Three of the procedures were selected for validation. The first using a QuEChERS based on the European Standards CSN EN 15662 [1], combined with a dispersive solid phase extraction (dSPE) clean-up specific for lipid elimination - the Enhanced Lipid Removal (EMR-lipid) dSPE by Agilent Technologies. The second and third ones were based in the official AOAC QuEChERS method [2] combined with two different dSPE clean-ups containing zirconium (Z-sep+ bulk) and carbon, respectively, as sorbents. These clean-ups were selected in order to eliminate complex matrix interferences, such as lipids and proteins. Samples were analysed using high performance liquid chromatography-mass spectrometry (HPLC-MS/MS) with an Exion LC AD coupled to a Sciex QTRAP 6500+ mass spectrometer. Results showed limits of detection ranging 0.26 to 22.49, 0.13 to 23.25 and 0.22 to 28.67 ng/g for EMR-lipid, zirconium, and carbon, respectively. Matrix effects were also calculated ranging -54 to +49, -70 to +51 and -63 to +15 % for EMR-lipid, zirconium, and carbon, respectively. The three methods achieved satisfactory recoveries, most of them ranging 60-120%. There were some exceptions, such as the pharmaceutical metformin, which recoveries were <10% for the three methods and the illicit drug 4-MeO-PCP, which was satisfactorily recovered just with the carbon clean-up. Based on the results of this study, we concluded that the simple changes made to the classic QuEChERS method can improve the overall recoveries for many types of different contaminants without sacrificing the performance of a multi-residue method.

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QUALITY CONTROL OF N-NITROSAMINES IMPURITIES IN PHARMACEUTICAL PRODUCTS USING DISPERSIVE LIQUID-LIQUID MICROEXTRACTION AND GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Nitrosamines (NAs) are chemicals catalogued as potential human carcinogens, specially, N-nitrosodimethylamine (NDMA) and N-nitrosodiethylamine (NDEA). The formation of NAs in pharmaceutical products is associated with the synthesis process [1]. This study describes the development and validation of a general procedure for the determination of nine NAs (NDMA, N-nitrosomethylethylamine (NEMA), NDEA, N-nitrosopyrrolidine (NPYR), N-nitrosomorpholine (NMOR), N-nitrosodi-n-propylamine (NDPA), N-nitrosopiperidine (NPIP), N-nitrosodi-n-butylamine (NDBA) and N-nitrosodiphenylamine (NDPhA)) useful for the quality control of pharmaceutical products using dispersive liquid-liquid microextraction (DLLME) and gas chromatography-mass spectrometry (GC-MS). A mixture containing 0.5 mL methanol and 150 µL chloroform as dispersant and extractant solvents, respectively, was added to the aqueous phase (1 g of product in 10 mL of water). The organic phase collected at the bottom of the conical tube was analysed using a 20 min oven programme in the GC-MS system. Quantification limits were between 0.21-21 ng g^{-1}, corresponding to NDPhA and NDMA, respectively. Adequate precision of the method was achieved with relative standard deviations lower than 12%. This combination of techniques provides high sensitivity with a rapid and easy sample treatment; therefore, it could be of relevance in the field of pharmaceutical quality control for determining carcinogenic impurities associated to the synthesis processes.

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MAGNETIC MOLECULARLY IMPRINTED POLYMER FOR THE EXTRACTION OF PHENOXYACID HERBICIDES FROM ENVIRONMENTAL WATER SAMPLES

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Phenoxyacid herbicides have been widely used in agriculture since the 1950s to control annual and perennial broadleaf weeds in a wide range of crops. Due to their high solubility in water and low sorption in soil, these herbicides have been frequently detected in surface water, although they can also permeate into groundwater. Hence, these compounds can enter into the human food, which implies a significant health risk due to their endocrine activity [1]. These herbicides are present in aqueous systems at trace levels, which makes sample pre-treatment mandatory for both pre-concentration of compounds and removal of matrix interferences. The interest in magnetic solid-phase extraction (MSPE), a type of SPE based on the use of magnetic sorbents, has increased in the last decades due to its well characteristics such as high adsorption efficiency, easy operation and fast separation. In order to enhance the selectivity of MSPE sorbents, the combination of magnetic nanoparticles with molecularly imprinted polymers (MIPs), made with an adequate template molecule, has become a versatile and highly selective tool in environmental analysis. In this study, a magnetic MIP (MMIP) that allows the selective and sensitive extraction of five phenoxy herbicides has been synthesized. The MMIP was prepared by thermal polymerization using amino functionalized magnetic nanoparticles as host support, and 4-chloro-2-methylphenoxyacetic acid (MCPA) herbicide as template, 4-vinylpiridine as functional monomer, ethylene glycol dimethacrylate as cross-linker, and acetonitrile as porogenic solvent. The non-imprinted magnetic polymer (MNIP), synthesized in the absence of MCPA, was used as reference polymer. The optimum conditions for the MSPE procedure (adsorption and desorption time, washing solvent, eluent volume and type, and breakthrough volume) have been established, and their applicability has been proved by the extraction of these herbicides from environmental water samples from different sources.

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DEVELOPMENT OF POLYMERIC MATERIALS MODIFIED WITH DIFFERENT GALACTOSE DERIVATIVES FOR SELECTIVE EXTRACTION OF PHYTOHEMAGGLUTININ FROM VEGETABLE MATRICES

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Phytohemagglutinin (PHA) is a toxic lectin, which is present in many varieties of beans, but is highly abundant in red kidney beans. Indeed, it has been reported that these beans and other related legumes have demonstrated to induce allergic manifestations after consuming these allergic foods in allergic individuals [1]. The extraction of PHA from vegetable samples is often complicated and it requires many purification steps (such as precipitation, affinity and ionic chromatography, among others) [1,2]. These methodologies are time-consuming and expensive, leading to a low yield of the entire process. PHA shows a carbohydrate-binding affinity (particularly for N-acetylgalactosamine/galactose sugar moieties), being able of inducing hemagglutination by recognizing erythrocyte surface glycoconjugates [1]. Taking advantage of this affinity, different polymeric materials modified with galactose derivatives to be used as sorbents in solid-phase extraction (SPE) of PHA from vegetable matrices, have been developed in this work. For this purpose, glycidyl methacrylate (GMA)-based monoliths were prepared and modified using two different approaches. In the first one, the GMA-based polymer was modified with ethylenediamine and glutaraldehyde and next functionalized with two different galactose derivatives. In the second approach, the starting polymer was modified with cystamine, and next functionalized with gold nanoparticles, on which a thiolated galactose derivative was subsequently immobilized. The resulting materials were characterized and tested as SPE phases for extraction of PHA. The sorbent that provided the largest PHA retention was then selected and it was investigated in terms of extraction efficiency. The PHA content collected in the different fractions of these steps was evaluated by HPLC after derivatization with fluorescein isothiocyanate (FITC). The experimental conditions of formation of PHA–FITC derivative and its HPLC separation were also optimized. Using the best conditions, the developed sorbent was applied to the extraction of PHA present in the vegetable matrices followed by its analysis both by SDS-PAGE and HPLC.

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PAPER-BASED FLUOROGENIC APTASENSOR FOR DETECTION OF CONCANAVALIN A IN FOOD PRODUCTS

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Concanavalin A (Con A) is a carbohydrate-binding protein that has strong affinity for mannose and glucose moieties on glycoproteins and glycoconjugates. This protein is commonly present in plants, being mostly located in seeds, raw legumes and tubers, among others. This dietary lectin acts as antigen to human glycoproteins and it can causes allergic responses upon its ingestion by a normal or an allergic individual [1]. Therefore, their determination in food products is necessary to prevent the allergic responses and associated complexities in sensitive or allergic people. Apart from classical agglutination assays, Con A evaluation has been performed using ELISA and immunoelectrophoresis assays. However, these antibody-dependent assays are often costly due to the requirement of live hosts for antibody production. In the last years, aptamer-based biosensors (aptasensors) have been developed as promising tools, in which aptamers are intelligently designed and applied as biological recognition elements with superior features (in vitro synthesis, easy modification, large thermal tolerance) compared with antibodies. In particular, fluorescent aptasensors have received substantial attention to determine different species (such as metal ions and large biomolecules) due to low cost, rapid detection, wide response range and facile operation [2,3]. Within species that can be used to design the aptasensing assays, the use of graphene oxide (GO) (as inorganic quencher) has received particular attention due to its unique features (cost-effective production, biocompatibility, desirable water-solubility, high chemical stability, large surface area, etc). In this work, a highly sensitive and selective paper-based aptasensor to detect Con A using a fluorescent based on a GO fluorescence sensing platform was developed. In order to achieve the highest efficiency of the aptasensor, several parameters (such as the volume of the aptamer and GO solutions on the test zone, their concentration, incubation time, among others) were optimized. The figures of merit of the developed aptasensor were also established and it has been successfully applied to determine this protein in food samples. Additionally, a simple and rapid smartphone-based portable assay was developed, which can serve as a potential diagnostic tool for home monitoring of Con A in food products.

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MAGNETIC DISPERSIVE MICRO-SOLID PHASE EXTRACTION COUPLED TO ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY FOR THE SPECIATION OF SILVER AND GOLD

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The intensive use of metallic nanoparticles leads to their presence in water at very low concentrations, so sensitive analytical procedures are required for their determination. Thus, for the relevant case of silver nanoparticles, AgNPs, single-particle inductively coupled mass spectrometry has been used for the purpose [1]. This is an excellent technique, but its high price makes it unaffordable for many laboratories. The required performance, including the possibility of discriminating the metallic particles from the soluble ions, can be also achieved by means of electrothermal atomic absorption spectrometry coupled to a preconcentration stage. Strategies in this regard have employed liquid-liquid [2] or solid-liquid [3-4] microextraction techniques. The results reported to date following this approach usually require two independent measurements, one of them providing the total Ag present, while the discrimination between AgNPs and Ag(I) species is based on the difference between the two measurements.

A very sensitive procedure is presented here that allows this speciation by using dispersive solid-phase microextraction with a simple magnetic material that obviates the need for a centrifugation step. The magnetic ferrite particles are not functionalised but used directly. Speciation is based on two independent measurements. At pH 4 the monovalent species is retained, while at pH 8 it is the metallic nanoparticle that is retained on the magnetic material. There is no measurement by difference, always prone to a greater uncertainty in the results. The process is very fast, and an enrichment factor close to 100 is achieved. The results obtained with certified reference materials support the reliability of the procedure. A similar methodology also achieves the speciation of gold nanoparticles and their soluble species.

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EFFECT OF TRICLOSAN EXPOSURE ON STEROIDOGENESIS IN FEMALE RATS THROUGH ANALYTICAL PROCEDURES BASED ON MASS SPECTROMETRY

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Triclosan (TCS) is an active ingredient in personal care products used to prevent the growth of fungi and bacteria. The U.S. Food and Drug Administration indicated that the use of TCS does not yet have conclusive results regarding its safety and effectiveness [1]. Current experimental evidence regarding in-vivo and in-vitro studies reflects that TCS is an endocrine disrupting compound (EDC), although the data remains incomplete and contradictory. Alterations in steroidogenic enzymatic activity, disruption of hormonal metabolism, displacement of hormones from its receptors have been proposed as possible disruption mechanisms of action of TCS [2]. Due to the incongruities previously reported by exposure to TCS, it is important to continue studying its effect on the endocrine system, including sex hormones, and the process of activating the secretion of these hormones through the action of kisspeptins. Kisspeptins are a family of neuropeptides encoded by the KISS1 gene, secreted mainly by the hypothalamus and they have a key action as regulators of GnRH neurons [3]. In-vivo studies generally involve immunoassays, but in this research, it was proposed to study the effect of exposure to TCS in rats through mass spectrometry and to compare it with commercial immunoassays.

Fourteen female adult Sprague-Dawley rats (two months old) were subjected to the study with a TCS dose of 50 mg/kg/day for 28 days through intragastric gavage. Daily weight and estrous cycle were checked. In the serum of rats, the levels of sex hormones and kisspeptin were determined through mass spectrometry and immunoassays. Among some results it was found that rats exposed to TCS grew less than control rats (approx. 6% less) and no alterations in estrous cycle were found. It was confirmed by mass spectrometry that the levels of serum hormones were significantly decreased after 28 days of exposition (about 30%), however no significant differences were found in any of the groups studied when immunoassays were applied. Finally, although the decrease in hormone levels, no changes were observed in serum kisspeptin concentration. These results indicate that exposing adult female rat to TCS reduces of the steroidogenesis, leading to deficits in endocrine and reproductive function.

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HEADSPACE-SPME AS A VERSATILE MONITORING METHOD FOR DETECTION OF EARLY INSECT INFESTATION IN RICE

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Stored rice can be infested by a variety of insect pests that cause grain damage and reduce grain quality leading to grain storage losses of 9% in developed countries and even larger worldwide.[1] Modern stored-product integrated pest management (IPM) programs represent a more environmental and safe approach versus chemical insecticides for pest control. IPM makes decisions using knowledge of population dynamics and threshold insect density, where grain probe traps that target adult insects are used as a conventional method for monitoring insect densities.[2- 4] However, an adult female insect can produce hundreds of eggs before being detected which could delay pest control actions and increase the risks of grain losses. [1] Specific volatile organic compounds (VOCs) have been detected and identified as insect biomarkers for detecting the presence of a distinct insect.[1, 5, 6] Thus, the use of new monitoring methods for early insect detection would be highly beneficial for fine-tuning and improving IPM programs. In this regard, headspace monitoring technologies that allow the detection of specific VOCs in the store grain resulting from the activity of the larvae in early stages of insect infestations are needed in IPM programs. Several studies had identified VOCs such as benzoquinones, hydrocarbons, alcohols, furans, and aldehydes as insect biomarkers. [5-8] Specifically, isopentenols and polysulfides have been reported as potential early biomarkers for the presence of moths and beetles in rice. The aim of this study was to develop a headspace solid phase microextraction (HS-SPME-GC-MS) method for high-throughput analysis and detection of early volatile biomarkers (prenol, prenal, isopentenol, hexanal, dimethyl disulfide, dimethyl trisulfide, 2-methylfuran, and 2-pentylfuran) in rice. After examination of four commercially available SPME coatings, Carboxen-PDMS coating was found to be most effective in the extraction and desorption of the volatile components compared to the other fibers. We demonstrated that HS-SPME can be used as a fast and versatile insect monitoring technology in IPM programs.

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AN AUTOMATED ON-LINE SORBENT EXTRACTION PLATFORM AS A FRONT-END TO INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY FOR A NOVEL SOL-GEL FUNCTIONALIZED SILICA SORBENT

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Trace metals are continuously released in the environment through natural and anthropogenic processes. As a result, the monitoring of toxic and nutrient elements in environmental samples has aroused considerable concern [1]. In this study, an automated on-line sample separation and/or preconcentration platform based on sol-gel technology [2] was developed as a front-end to inductively coupled plasma atomic emission spectroscopy. The proposed system was prepared by packing a novel sol-gel functionalized silica sorbent in an easy repacking microcolumn format and it was coupled to ICP-AES for the simultaneous determination of cadmium, lead, copper, chromium, cobalt, nickel, zinc, manganese, mercury, and vanadium. The chemical and hydrodynamic parameters affecting the performance of the proposed method were thoroughly investigated and optimized. Under optimum conditions, the limits of detection and the limits of quantification for the target analytes were 0.05-0.24 μg L^{-1} and 0.17-0.79 μg L^{-1}, respectively. The precision of the proposed method was expressed in terms of relative standard deviation (RSD%) and ranged between 0.8% and 7.9%. Moreover, good accuracy was observed from the analysis of three certified reference materials. Finally, the herein developed platform was successfully employed for the analysis of environmental water samples.

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FAST AND SIMPLE SYNTHESIS OF PAPER-BASED MOLECULARLY IMPRINTED POLYMERS BY LASER POINTER-ASSISTED ACTIVATION

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Molecular imprinting technology is a technique used to design solid molecular recognition materials capable of mimicking natural entities such as antibodies or biological receptors [1]. The great success of molecularly imprinted polymers (MIPs) lies in advantages such as: high selectivity and specificity by the template molecule; chemical, mechanical, and thermal stability; and versatility. MIPs are mainly focused on the development of selective sorbents for solid-phase extraction approaches; however, the use of paper-based MIPs has been increasing in the last years [2], due to easy handling and incorporation into other devices. In this study, a quick, simple, and versatile strategy has been proposed for the synthesis of paper-based MIPs by bulk polymerization over a piece of nitrocellulose.

The polymerization solution, a mixture of methacrylic acid, ethylene glycol dimethacrylate, template and porogen, was deposited onto a piece of nitrocellulose paper. Photoactivation of the polymerization solution was carried out using the radical initiator Irgacure 819 and a 405 nm laser pointer for 10 minutes. Different manifolds, polymerization mixtures, and initiation times were evaluated in order to achieve an homogeneous layer over the nitrocellulose paper. The extraction efficiency of the nitrocellulose paper-based MIP was compared with a non-imprinted polymer, showing an improved performance. Therefore, the use of laser pointers to activate polymerization mixtures provides a promising strategy for the rapid, easy, and versatile synthesis of paper-based MIPS.

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MICROEXTRACTION BY PACKED SORBENT, A RELIABLE APPROACH FOR THE EXTRACTION OF NEW PSYCHOACTVE SUBSTANCES IN BIOLOGICAL FLUIDS

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New psychoactive substances (NPS) are continuously introduced in the market with slight structural modifications to conventional drugs, being amphetamine-type stimulants, synthetic cannabinoids, synthetic cathinones, and phenethylamines the largest categories found in the market [2]. Abuse drug consumption analysis is typically carried out in plasma, serum, and urine. Common analytical methods for the analysis of abuse drugs in biological fluids are based on liquid-liquid and solid-phase extraction, followed by gas or liquid chromatography–mass spectrometry determination [2]. A procedure for the determination of synthetic cannabinoids, tryptamines, methylone, and dichloropane has been developed based on microextraction by packed sorbent (MEPS) followed by ion mobility spectrometry (IMS) and gas chromatography-mass spectrometry (GC-MS) determination. The combination of MEPS with IMS determination provided promising advantages for in-field screening of NPS in oral fluids and urine, due to its simplicity, automation, and portability; while GC-MS determination was proposed for rearguard confirmatory purposes. The effect of sample pH and ionic strength, number of loading steps, and number of elution steps using different elution solvents were evaluated. The proposed procedure was validated in terms of linearity, sensitivity, selectivity, trueness, and precision. The obtained limits of quantification were from 14 to 120 µg L^{-1}; precision, calculated as the relative standard deviation of five determinations, was lower than 9 %.; and recovery studies were in the range of 66-110 %. Thus, the developed methodology can be considered a promising alternative to conventional analytical methods for in-field abuse drug consumption detection.

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DUAL MIXED-MODE POLY (VINYLPYRIDINE - CO - METHACRYLIC ACID - CO- ETHYLENE GLYCOL DIMETHACRYLATE)-BASED SORBENT FOR ACIDIC AND BASIC DRUG EXTRACTION

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Conventional reverse phase sorbents have been used for drug extraction in biological samples [1]. However, these sorbents show certain problems such as their instability at extreme pH as well its low ability to retain polar compounds and ionic drugs [2]. In this study, a simple and practical method for the synthesis of dual mixed-mode polymer sorbent via one-step thermally initiated polymerization of 4-vinylpyridine (VP), methacrylic acid (MAA) and ethylene glycol dimethacrylate (EGDMA) has been described for the solid-phase extraction (SPE) of basic and acidic drugs. The use of VP and MAA as ionizable functional monomers allowed the tailoring of ion-exchange and hydrophobic features of the polymer. The obtained polymer was characterized by Fourier-transform infrared spectroscopy and scanning electron microscopy. The retention behavior of dual mixed-mode polymer towards basic and acidic drugs was investigated. The results revealed that ion-exchange, hydrogen bonding, and hydrophobic interactions were present in the retention process of target analytes. In particular, the ion-exchange contribution can be switched reversibly between anion- and cation-exchange by a simple control of the pH of loading solution. The applicability of the developed sorbent was evaluated for the SPE of cocaine, 3-MMC, and diazepam in oral fluid samples followed their determination by ultra-high performance liquid chromatography tandem mass spectrometry. The method showed excellent recoveries and LODs in the range of 0.12 - 0.32 µg L^{-1} and exhibited better capability for these drugs than commercial sorbents (ExtraBond® Drug). Recovery values (at different spiked levels in blank oral fluid samples) were from 69 to 99 %. Thus, the results provided here afford valuable information for the development of new analyte-oriented sorbent design to face up challenging issues as enhanced selectivity in analytical applications.

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SILICONE-BASED SORPTIVE EXTRACTION OF ABUSE DRUGS IN WASTEWATER

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Silicone has been widely used as sorbent for the development of extraction techniques, mainly solid phase microextraction, but also in other approaches such as, stir bar, silicone rod and silicone tube sorptive extraction [1]. These extraction approaches show many advantages like lower extraction time and solvent consumption, and high extraction efficacy, compared to conventional ones. In this study, a silicone-based extraction technique has been developed for the extraction of abuse drugs from wastewater samples, including conventional ones and new psychoactive substances, determined by ultra high-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS-MS). Diverse silicone materials were evaluated to provide a fast and quantitative extraction of abuse drugs, including sheet and tubes of different dimensions. Moreover, the effect of sample pH and ionic strength, extraction and desorption times, type of shaking, and elution solvent was also evaluated. The proposed procedure was validated in terms of linearity, sensitivity, selectivity, trueness, and precision. The use of silicone-based sorptive extraction, combined with the high sensitivity and selectivity provided by UHPLC-MS-MS, allowed to reach very low detection limits with values lower than 1 µg L^{-1}. Thus, the developed procedure can be considered as a reliable alternative to conventional extraction methods for the determination of abuse drugs in wastewater and sewage treatment plant samples.

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SUPRAMOLECULAR SOLVENT-BASED MICROEXTRACTION PROBE FOR FAST DETECTION OF BISPHENOLS BY AMBIENT MASS SPECTROMETRY

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Ambient mass spectrometry (AMS) has emerged as promising techniques for fast screening of organic compounds. AMS consists in modified atmospheric pressure ionization sources, where solid o liquid samples are directly introduced (without previous preparation or chromatography separation) so that analytes desorb from the matrix and enter the MS detector.[1] In this study we investigated the suitability of supramolecular solvent(SUPRAS)-based microextraction probe for the development of generic and fast sample treatment prior to AMS analysis based on ASAP (atmospheric solids analysis probe). SUPRAS are nanostructured liquids formed by the self-assembly of amphiphilic aggregates with multiple binding sites and microenvironments of different polarity for efficient extraction at low volumes. [2] In ASAP, the solid or liquid sample is directly injected on disposable glass probes onto a modified atmospheric pressure chemical ionization (APCI) source. SUPRAS made up of fatty alcohols of different chain length (C6-C10) in mixtures of water and ethanol or tetrahydrofuran were tested to improve the sensitivity and selectivity of ASAP, to generate reproducible and integrable signals for data processing and to reduce cross-contamination. All these aspects are crucial to extent the applicability of AMS to routine analysis. The method was applied to the screening of bisphenol A and six structural analogues in thermal paper and food contact materials. Optimal results were achieved with SUPRAS synthesized with 1-decanol in mixtures of ethanol: water. SUPRAS (0.5-2 µL) were loaded onto glass probes that were placed in contact with samples for 5 seconds before ASAP analysis. AMS integrable peaks (0.2-0.5 min) were obtained with relative standard deviations of 2-25%. The method was applied to 62 samples of thermal paper and 14 samples of food containers from Spain. The results showed that BPA and BPS were the most widely used bisphenols in thermal paper and BPS in food packaging products, which suggests the increasing industrial replacement of BPA by BPS.

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THE PERFLUOROALKYL SUBSTANCES IN FISH FROM LAKES LOCATED IN EASTERN EUROPE

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This work contains an important information on the occurrence of perfluoroalkyl substances (PFASs) in selected tissues from pike (Esox lucius (L.)) and roach (Rutilus rutilus (L.)) both collected from two lakes located in the Masurian Lakeland (Poland) in Eastern Europe known as a one of the cleanest region in Europe with low level of pollutants. PFASs have been widely detected in living organisms, and exposure to these compounds increase risk of genotoxicity, immunotoxicity, neurotoxicity as well as carcinogenesis. Less is known on the presence of perfluoroalkyl substances in seafood and fish (freshwater/marine). The latest are a key component of healthy and well-balanced diet and provides essential nutrients to the body and are indicated as the most relevant source of PFASs. Therefore, due to the high need for human health risk evaluation arising from contaminated fish consumption, it is crucial to study the levels of PFASs in fish tissues. Ten PFASs were analysed in tissue of brain, liver, kidneys, gonads and muscles by micro-HPLC-MS/MS. The only perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA) and perfluorodecanoic acid (PFDA), were detected above LOQ. ΣPFASs concentrations was estimated to (Ełckie Lake/Hańcza Lake): 13.779/26.732 ng/g ww and 4.378/3.181 ng/g ww for pike and roach, respectively. The contribution of PFOS and PFOA to ΣPFASs was higher than those from the other analysed compounds. PFOS was found to be predominant in fishes from Ełckie Lake whereas PFOA in Hańcza Lake. It was noted that PFASs concentrations in the tissues declined in the following order kidney>gonads≈brain>liver>muscle. The sum (Σ) of PFASs estimated in pike kidneys from Hańcza Lake was the highest (9.656 ng/g ww). The information provided in our study makes better understanding of existing environmental dependencies in PFASs distribution and accumulation in biota.

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MONTHLY ASSESSMENT OF VOLATILE METHYLSILOXANES IN BEACH SAND

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Volatile methylsiloxanes (VMSs) have outstanding properties that reflect their intensive use in a considerable number of domestic and industrial applications [1]. Personal care products (PCPs) are an example and one of the main vehicles for the presence of VMS in coastal areas. In these locations, beach sand can provide important information regarding the distribution of VMSs, namely on possible seasonal or geographical trends [2]. In this study, three linear (L3-L5) and four cyclic (D3-D6) VMSs were analysed in sands from twelve different beaches in the North and Center of Portugal, using a fast, easy, cheap, effective, robust and safe extraction method (QuEChERS) [3], followed by quantification by gas chromatography coupled with mass spectrometry (GC-MS). Individual VMSs were detected in all samples analyzed, with concentrations between <LOQ and 27.6 ng/g, with an average of 1 ng/g. Cyclic VMSs, namely D6 and D5, were detected with higher frequency and concentration than the linear ones, of which only L5 was detected above the LOQ. Although there was no trend related to the geographical location of the beaches, in general it was found that the summer months had higher levels of contamination, which is most likely related to the greater influx of sunbathers and tourists.

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METALS PRESENT IN CRUMB RUBBER USED AS INFILL OF SYNTHETIC TURF PITCHES

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An End-of-Life Tire (ELT) is a tire that can no longer be used on vehicles, being mostly redirected for recycling or energy recovery (incineration) [1]. Synthetic turf pitches are a major end-market of this material, in which ELTs-derived crumb rubber is used as infill [1]. However, this can raise environmental concerns, since harmful chemicals contained in rubber, such as polycyclic aromatic hydrocarbons and metals, are easily released from the pitches to the surroundings (water, air & soil) [2]. In the case of metals with toxic effects (*e.g.* Zn), previous studies report their occurrence in crumb rubber at relevant concentrations [3], becoming pertinent the assessment of this class of contaminants in this matrix. In the present study, a total of 103 crumb rubber samples collected from football pitches of 13 countries were analyzed for the presence of 29 elemental species. A microwave-assisted digestion protocol with HNO_3 was used to prepare samples for analysis by ICP-OES. Results revealed a wide concentration range for each metal, suggesting that metals were not uniformly distributed. However, Zn was consistently the most abundant element, with an average concentration of 4041 ± 447 mg/kg, which is highly above the limit stablished in similar materials (3750 mg $_{Zn}$/kg in dry, brittle, powder-like or pliable toy material, Directive 2009/48/EC). In fact, Zn levels accounted for 66%, on average, of the total concentrations in all samples, followed by Fe (9%), Mg (7%) and Al (7%). These observations are coherent with what is reported in similar studies and reflect the need of metals monitorization in sites containing ELT-derived crumb rubber.

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OCCURRENCE AND HUMAN EXPOSURE TO VMS IN THE INDOOR AIR OF DIFFERENT LOCATIONS

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Volatile methylsiloxanes (VMSs) fulfill the needs of several industries, being extensively used in cosmetic and personal care products (PCPs). Due to their volatile character, the majority of these compounds are released to the atmosphere during their manufacture, use, and disposal. Once there, they can be subjected to long-range transportation, likely affecting distant populations. Their atmospheric fate is object of study due to their bioaccumulative potential in ecosystems and plausible toxic effects in humans [1]. However, the literature focused on the indoor presence of these compounds is still sparse, and some environments, such as paint warehouses, stationery shops, and dentists, have not been studied yet. The present study aims to measure the levels of VMSs in the indoor air of different environments, identifying possible sources of contamination, and estimating the human exposure and health risk of VMSs inhalation. To do this, passive air samplers containing XAD-2 sorbent were deployed in over 20 different indoor spaces. After two weeks, the sorbents were collected and extracted in separation funnels with hexane, in a procedure adapted from Krogseth et al. [2]. Three linear (L3-L5) and four cyclic (D3-D6) VMSs were quantified by GC-MS. Finally, the human exposure to VMSs was calculated for adult males and females according to the guidelines provided by Anh et al. [3]. Preliminary results show total VMSs levels ranged from 14.09 to 0.03 µg/day, obtained in a private bedroom and a boat workshop, respectively. Exposure values between 101.4 and 0.08 µg/kg·day were obtained, depending on the location and population group assessed.

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PARTITION OF VMS AMONG THE MATRICES OF WWTP METHANOGENIC DIGESTERS

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Volatile methyl siloxanes (VMSs) are a group of organosilicon synthetic products used mostly as moisturizers and emollients in cosmetics and personal care products (PCPs) formulations [1]. After their application, these compounds can volatilize easily. However, residues of them arrive to wastewater treatment plants (WWTPs) via wash-off waters. Once there, they partition among the different matrices present in these installations depending on their solubility and volatility. A significant portion of VMSs reaches the sludge, and, if digested, ends up in biogas, compromising the quality of this resource. A few studies have monitored VMSs in the water and sludge lines of different WWTPs, but no studies are found focused on the dynamics occurring in biogas digesters [2]. To surpass this gap, this work aims to generate a mass balance of VMSs within these installations. To do so, samples of entry and digested sludge, as well as produced biogas, were taken from several digesters. Subsequently, VMSs present in the sludge were extracted by liquid-liquid extraction with n-hexane, before GC-MS quantification, while biogas was directly analyzed from sampling bags by means of a GC-IMS-SILOX. Preliminary results show that the average removal of total VMSs from the entry sludge was 47%, reaching, at some locations, values up to 98%. This mass of siloxanes was transferred to biogas, reaching levels of total VMSs above 5 mg/m^3 (limit recommended by some internal combustion engine manufacturers [3]). Regardless of the WWTP and the matrix (i.e. sludge or biogas), decamethylcyclopentasiloxane (D5) was the dominant VMSs.

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AUTOMATION BY FILTRATION AND AUTOMATIC DILUTION OF SAMPLES IN ION CHROMATOGRAPHY

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"Clean and free of particles"; this would be the description of the ideal sample for Ion Chromatography. But the truth is that the samples that arrive at our laboratories tend to be very different. Several steps are necessary to achieve optimal sample preparation in Chromatography, while protecting the separation column that guarantees the durability and correct operation of the IC system. This work consists of developing and validating an automatic filtration and dilution method. **In-line sample preparation** opens new fields of application as it allows the highly reliable elimination of sources of contamination, facilitating **ultra-trace analysis** and **eliminating the manipulation of the sample** by technical personnel. It is essential to pay special attention to the precision and accuracy of the method. To achieve this, a digital burette (Metrohm patented Dosino 800) is used. It is a dosing system that allows liquids to be quickly aspirated and dosed with extreme accuracy and with a precision of 0.2µl. Obtaining both a calibration line directly from a single commercial standard and the automatic dilution of the samples, eliminating any interference from accessory elements (such as traces of impurities in a sample beaker when performing the dilutions externally). It includes an advanced rinsing system (set in the same analysis method) that prevents any spread of impurities between samples and prevents clogging of the filter in the case of analysis of samples laden with organic matter. Dilutions will be made so that the expected analytes fit within the established range of our calibration line. And all this while the sequence lasts and without losing workflow. This technique reduces manual steps, is very robust, reliable and requires little maintenance by the technical personnel.

There are other techniques that offer good results in the analysis of water by Chromatography. However, the results obtained in our daily work, after years of experience with samples from very different sources and a high level of interferences, show that **the method described for online sample preparation is the most recommended**.

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A CYCLODEXTRIN-SILICA COMPOSITE AS A SORBENT FOR THE EXTRACTION OF SYNTHETIC CANNABINOIDS FROM SALIVA

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New designer drugs have been a major issue concerning law enforcements during the last few years due to the high amount of structures seized and characterized [1]. In this sense, different extraction techniques have been developed to extract these molecules selectively from human fluids [2].

A silica-cyclodextrin composite for the solid-phase extraction of synthetic cannabinoids (ADB-CHMICA, MMB-CHMICA, and MDMB-CHMICA) from human saliva is proposed here. Recoveries reach up to around 100% and around 80% when working with both water and real saliva, respectively. The limits of detection and quantification have been established at the ng L^{-1} level. The same kind of material without cyclodextrin has been also synthesized and applied for the same extraction procedure, showing significantly minor recoveries. This justifies, then, the presence of cyclodextrin. Additionally, the effect of possible interferences (specifically tobacco, syrup, coffee, and candy) has been studied. Results imply that the analyst is still able to identify a positive sample when three out of these four mentioned are present in the matrix.

Overall, this work shows that cyclodextrin represents a powerful tool that may be applied in the New Psychoactive Substances extraction protocols due to its versatility and potential interactions with this kind of drugs.

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EXTRACTION OF ORGANOPHOSPHORUS FLAME RETARDANTS IN WATER SAMPLES USING TITANIUM HIERARCHICAL POROUS SILICA MATERIALS AS SORBENTS

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Flame retardants (FRs) are chemical additives widely used to prevent combustion or delay fire propagation. Since these additives are not chemically bonded to the product they can be easily released to the environment. For this reason, these compounds are currently considered as emerging pollutants, being an ongoing global concern regarding public health [1]. Indeed, high concentrations of these emerging pollutants were found in Valencia (Spain), being the major source of polluted water the wastewater treatment plants [2].

In this work, a sorbent for the extraction of organophosphorus flame retardants has been proposed, based on UVM-7 mesoporous silica doped with titanium. Designed cartridges have been applied to the extraction and preconcentration of flame retardants in water samples, followed by gas chromatography coupled to a mass spectrometry detector. Firstly, UVM-7 materials with different contents of titanium were synthesized and characterized by several techniques. The potential of these materials was assessed in comparison with their morphological properties, resulting Ti50-UVM-7 the best solid phase. Several extraction parameters were also optimized. Analytical parameters were also evaluated, and limits of detection from 0.019 to 0.21 ng mL^{-1} were obtained, as well as intra-day relative standard deviation below 11% for all analytes. Extraction efficiencies above 80% in water samples were achieved. The reusability of the material was also proved. Finally, the designed protocol was applied for the analysis of real water samples, and quantifiable concentrations of TCIPP, TDCIPP, and TPhP were obtained in some samples.

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DETERMINATION OF Ag, Cu AND Pd BY MEANS DISPERSIVE LIQUID-LIQUID MICROEXTRACTION AND INDUCITVELY COUPLED OPTICAL EMISSION SPECTROMETRY USING A TASK-SPECIFIC IONIC LIQUID

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There is a great concern worldwide about the presence of element impurities in foods, pharmaceutical and environmental samples due to their negative impact on human health. Control of elemental impurities is usually performed by means atomic spectrometry techniques after a preliminary sample treatment step for sample decomposition (i.e. acid digestion) [1]. However, because the low levels of some impurities, an extraction/preconcentration step may be required for analyte detection as well as to reduce matrix effects [1,2]. Dispersive liquid-liquid microextraction (DLLME) has attracted extensive interest due to its simplicity and figures of merit [3]. Over the years, different extractant solvents and chelating agents have been employed for metal extraction in DLLME procedures. When compared to other solvents employed in the literature, ionic liquids are very attractive since they could be selectively customized by introducing chelating groups within their structure for selective metal extraction (i.e. task specific ionic liquids, TSILs) thus avoiding the use of an external chelating agent. Some preliminary experiments have shown that 1-butyl-2-(diphenylphosphino)-3-methylimidazolium hexafluorophosphate is a an efficient TSIL for Ag, Cu and Pd extraction. Therefore, the goal of this work is to develop a new analytical method for Ag, Cu and Pd determination in complex samples (environmental and pharmaceutical) using a TSIL-based DLLME procedure and inductively coupled plasma optical emission spectrometry detection.

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APPLICATION OF THIN-FILM MICROEXTRACTION TO ANALYSIS OF VOLATILE METABOLITES

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Volatile organic compounds (VOCs) have been proposed in the last two decades as biomarkers for disease detection and therapeutic monitoring. Substantial effort has been done to identify and quantify VOCs in diverse body fluids, such as blood, breath, urine and saliva. Nevertheless, the complete understanding of factors affecting their concentration patterns, particularly in relation to disease progression or resolution, is a formidable challenge. Therefore, it is crucial to elucidate whether given VOCs originate from normal human cells or pathogens, including bacteria, virus-infected cells, transformed cancer cells, etc. For this purpose, in vitro experiments with clean populations of microorganisms or cell cultures are essential. Due to the trace concentrations of target metabolites, being often at sub-ppb levels, adsorptive enrichment is needed before the GC-MS analysis. Solid-phase microextraction (SPME) proved to be a versatile technique for analytes enrichment in numerous medical, pharmacological and biochemical applications [1]. Using a planar mesh coated with stationary phase increases the extraction phase volume and active surface area, enabling Thin-Film Microextraction devices to reach lower detection limits and wider VOCs range compared to regular SPME fibers. In this study, four different adsorbents, all suspended into PDMS membrane, were compared as coating materials for TFME sheets: carboxen (CAR), divinylbenzene (DVB), hydrophobic−lipophilic balance (HLB), and pure polydimethylsiloxane (PDMS). Amongst them, the HLB sheets using poly(divinylbenzene-co-N-vinyl-pyrrolidone) skeleton structure were proved to be the most versatile, enabling the most sensitive analysis of VOCs with a broad polarity and volatility. For this sorbent, further conditions have been examined, including sampling type (internal static headspace, external bi-directional headspace, direct immersion), extraction time and extraction temperature. The usefulness of the here proposed method for analysis of trace-VOCs was ultimately demonstrated for A549 transformed cell lines as well as *Escherichia coli* strains isolated from critically ill patients suffering from ventilation-associated pneumonia.

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SENSITIVE ANALYSIS OF GLYCOPEPTIDES FROM GLYCOPROTEIN BIOPHARMACEUTICALS BY ON-LINE PHENYLBORONIC ACID SOLID-PHASE EXTRACTION CAPILLARY ELECTROPHORESIS-MASS SPECTROMETRY

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In this study is described an on-line solid-phase extraction capillary electrophoresis-mass spectrometry (SPE-CE-MS) method, using a phenylboronic acid (PBA) sorbent for the selective purification and preconcentration of glycopeptides from enzymatic digests of glycoproteins analysed in bottom-up proteomic approaches. Recombinant human erythropoietin (rhEPO) was selected as glycoprotein reference standard and subjected to enzymatic digestion with several proteinases. For PBA-SPE-CE-MS, a particle-packed microcartridge was integrated in-line near the entrance of the separation capillary and no valves were necessary for the operation. First, the sorbent was conditioned with binding buffer. Then, after loading the sample (~100 µL) and several washing steps, retained glycopeptides were eluted and glycopeptide glycoforms were separated and detected by CE-MS. The tryptic O126 and N83 glycopeptides from rhEPO were targeted to optimize the methodology. Several aspects that affect the selective retention and elution, peak efficiency and electrophoretic separation of the O126 an N83 glycopeptide glycoforms were investigated to maximize detection sensitivity while minimizing non-specific retention of peptides. Under the optimized conditions, repeatability, reproducibility, linearity, limits of detection and microcartridge lifetime were evaluated. Finally, the PBA-SPE-CE-MS method was also applied to the analysis of rhEPO glycopeptides from chymotripsin and endoproteinase Glu-C digests in order to increase detection sensitivity of N24 and N38 glycopeptides, compared to regular CE-MS, achieving a deeper characterization of several rhEPO biopharmaceuticals.

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ANALYSIS OF DRUGS OF ABUSE IN URINE AFTER CLEANUP WITH HLB SOLID PHASE EXTRACTION 96-WELL PLATES

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Supel™ Swift HLB SPE is a new, proprietary and patent pending copolymer having both hydrophilic and lipophilic functional groups. It is for use as a sorbent material in solid phase extractions (SPE) prior to instrumental analyses, such as LC-MS/MS. Supel™ Swift HLB's dual polarity nature makes it ideal for extracting a broad range of compounds from aqueous matrices and is appropriate for applications for food & environmental samples as well as biological samples such as urine, serum and plasma. The hydrophilic and lipophilic balance (HLB) property of the polymer material enables the retention of a wide range of compounds having a wide range of polarities and Log P values.

There are many benefits of polymeric SPE materials versus traditional silica based SPE materials including: the ability to accommodate a wider pH range of solvents and buffers, better flow rates and decreased backpressure, and greater capacity via higher surface area.

In this work, we demonstrate the ability to perform cleanup of urine samples using HLB solid phase extraction for the analysis of various opioids via LC-MS/MS. The 96-well SPE format utilized is optimal for clinical and other laboratories working in a high-throughput environment. This application demonstrates the effectiveness of the HLB material to produce clean samples resulting in accurate and reproducible data.

LC-MS ANALYSIS OF PHARMA COMPOUNDS IN PLASMA AFTER CLEANUP WITH HLB SPE CARTRIDGES

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The preparation of biological samples can have a large impact on the reproducibility and confidence in the results. Hydrophilic-Lipophilic Balanced (HLB) cartridges contain a sorbent which offers good wettability for hydrophilic compounds and the ability to provide reverse phase retention with the lipophilic phase. These properties allow HLB cartridges to effectively handle a broad range of compounds with varying properties. In this study, a mixture of twenty pharmaceutical compounds with ranging log P values of (-0.89 to 4.65) were analyzed from calf serum using Supel™ Swift HLB SPE cartridges.

The Supel™ Swift HLB SPE cartridges were demonstrated to produce excellent recoveries (100% of analytes in the range of 80-120%) and minimal ion enhancement effects for 80% of the analytes. The advantages of the Supel™ Swift HLB SPE cartridges were further demonstrated when comparing to another commercially available HLB cartridge under the same set of conditions.

DEVICE WITH A POLYMER INCLUSION MEMBRANE FOR PHOSPHATE MONITORING IN FRESH WATER AND WASTEWATER

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Phosphate is an inorganic anion commonly found in fresh waters, which originates from point sources (for example municipal landfill leachates, anaerobic digested sewage sludge, among others), as well as non-point sources (run-off from agriculture and pasture), and industrial activities. The presence of phosphate at high concentration cause eutrophication in surface water bodies, and consequently a severe reduction in water quality.

For phosphate monitoring purposes, different devices and sensors have been designed [1,2]. Donnan membrane technique (DMT) based on equilibrium measurements [3] has been used for cation and anion measurements in waters. The technique makes use of commercial ion exchange membranes placed in a specific field-cell. Other types of chemically functionalized membranes can be used with this field-cell in a regime of perfect sink accumulation. Polymer inclusion membranes (PIMs) are a type of functionalized membranes synthesized in the laboratory and composed by two main components: a polymer and a carrier. The polymer is the skeleton of the membrane providing mechanical strength, and the carrier is responsible for binding the species of interest by complexation or ion-pair formation. The application field of PIMs is very large, including separation of inorganic anions and cations, and organic compounds [4]. We present results from the application of PIMs containing the ionic liquid Aliquat 336 (trioctylmethylammonium chloride) in a DMT field-cell design for the monitoring of phosphate in fresh waters. The influence of some experimental parameters (deployment time, volume of donor solution) on the phosphate accumulation in the receiving chamber has been evaluated in model solutions. Then, the technique has been applied to natural surface waters and wastewater from the wastewater treatment plant in Girona (Catalonia, Spain).

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HT-BAµE: A NEW TOOL FOR MONITORING KETAMINE AND NORKETAMINE IN URINE SAMPLES

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Ketamine can be used as a recreational or "club drug" since is produces hallucinogenic and stimulant effects. Moreover, ketamine can also misuse as a "date-rape" drug (to induce amnesia in unsuspecting victims) [1]. For this reason, simple, fast, reliable, and cost-effective methods are needed for the determination of these compound in urine matrices.

Novel static-based microextraction techniques, such as bar adsorptive microextraction (BAµE), have demonstrated to be a very effective and alternative analytical tool for monitoring priority compounds in aqueous matrices [2]. However, this technique is not dedicated for high throughput analysis.

In this work, we present the development, optimization, validation, and application of a simple, fast, reliable and cost-effective sample preparation approach using high throughput bar adsorptive microextraction (HT-BAµE) in combination with gas chromatography-mass spectrometry operating in the selected-ion monitoring acquisition mode, for the simultaneous enrichment of ketamine and its major metabolite (norketamine) from a large number of urine samples.

The target compounds were extracted in a novel HT-BAµE apparatus [3], which allows for simultaneous microextraction and subsequent back-extraction of up to 100 samples, resulting in a sample preparation time of only 0.45 min/sample. Under optimized experimental conditions, the developed methodology allowed for linear dynamic ranges between 5.0 and 1,000.0 µg L^{-1} with determination coefficients of 0.997 and 0.999, as well as average recovery yields of 84.9-89.8 % and 96.5-97.8 % for norketamine and ketamine, respectively. The developed methodology was applied for the analysis of 24 samples (in triplicate), where no target compounds were detected (< LOD).

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DEVELOPMENT OF A PASSIVE SAMPLER FOR SAMPLING OF EMERGING POLLUTANTS IN WATERS.

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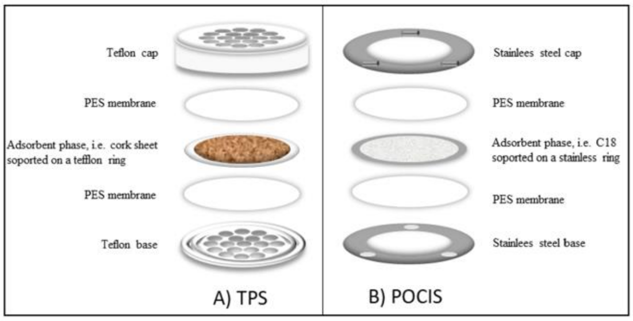
In this study we developed a Teflon Passive Sampler (TPS) that allowed evaluating the presence of various emerging pollutants in both natural water samples, as well as in effluents of the wastewater treatment plants in Santiago of Chile. Different natural and commercial sorbent phases were examined, concluding that the particulate and laminar cork phases are suitable for the sorption of the group of compounds under study, but considering the grinding and assembly time that is consumed in the preparation of the particulate phase, the choice of the laminar cork sorbent phase is recommended. Sampling rates (Rs) were obtained for some compounds studied under laboratory conditions for the laminar cork which varied between 0.620 Lday^{-1} for ethyl paraben and 19.013 Lday^{-1} for estrone. These pasive samplers were applied in two sampling periods carried out before and after the Trebal (Aguas Andinas) treatment plant, in spring 2018 and in winter 2019.



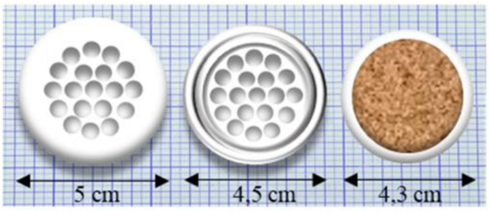


Figure 1. Configuration of (a) TPS developed (b) POCIS. Figure 2. Top view of TPS

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ASSESSMENT OF THE DEGREE OF CONTAMINATION AND SPATIAL DISTRIBUTION OF PRIORITY POLLUTANTS IN URBAN SOILS

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Urban soils are commonly polluted by organic and inorganic substances that may represent risks for human health and well-being, as well as for the functioning of the urban ecosystems, in which soils play a key role. Despite this, reports of contamination in urban soils in Spanish cities are still scarce. The main goal of this work is to determine the degree of contamination and spatial distribution of polycyclic aromatic hydrocarbons (PAHs), in more than 50 urban soils from Santiago de Compostela, Northwestern Spain, under different vegetations and land uses. Sample preparation was carried out by miniaturized ultrasound-assisted extraction (UAE), employing few amounts of sample and solvents. Analysis was performed by GC-MS/MS. The method was successfully validated in terms of linearity, accuracy, precision, and sensitivity, showing its suitability to detect trace levels of PAHs in soils. Results revealed the presence in soils of 17 out of the 18 target PAHs, with total concentration levels up to µg g^{-1} in 28% of the analyzed soils. The sum of their concentrations ranged between 4 and 4728 ng g^{-1}. The sum of the 16 EPA PAHs ranged from 4 to 4216 ng g^{-1}, similar to other similar-sized cities with low population densities. The presence of B[a]P, considered the most toxic PAH congener, at concentrations of several hundreds of ng g^{-1} was confirmed in several soils samples. A screening analysis was also performed to obtain a deep characterization of the soil contamination by organic compounds. In general, all PAHs were strongly intercorrelated except NAP, whereas no correlations have been found to soil physicochemical properties. The results of this work are very meaningful, providing very valuable information for the protection of urban soils, environmental and human health.

Acknowledgement.

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VOLUMETRIC DRIED URINE SAMPLING FOR THE ANTI-DOPING ANALYSIS OF SMALL PEPTIDES

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In the last years, the use of substances able to improve physical performance has become a widespread practice among both professional and amateur athletes. The World Anti-Doping Agency (WADA) annually draws a list of the prohibited substances with the aim of fighting and preventing the spread of doping [1]. Among banned substances in sports there are several endogenous compounds of peptide nature, for which a large use and diffusion has recently been observed. As a consequence, the development of reliable analytical methodologies is of utmost importance in order to effectively evaluate possible illicit intake. Routine anti-doping analyses are mainly performed on fluid urine samples, with some inherent issues related to sample handling, analyte stability and athlete compliance. The possibility to exploit dried urine microsamples as an alternative matrix is a promising strategy to overcome some of these problems in the future [2]. In this study, a volumetric absorptive microsampling (VAMS) approach for the evaluation of illicit peptide intake in urine is proposed. For each sample, an accurate urine volume (20 µL) was collected on porous polymeric device tips and then dried and stored at room temperature before pretreatment and analysis. The analytes were identified and quantified by means of an original UHPLC-HRMS method, fully validated with satisfactory results for example in terms of extraction yield (>77%), matrix effect (<8.1%) and precision (RSD <6.6%). The approach based on VAMS-UHPLC-HRMS developed herein proved to be a promising tool in the fight against doping in sports.

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IN-VITRO BIOAVAILABILITY OF MIGRANTS FROM MICROPLASTICS BY DISPERSIVE SPE USING LIPOSOME-BASED MAGNETIC COMPOSITES

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Plastic is the most ubiquitous pollution material in the environment and most of it ends up in the sea. Over time, plastic breaks up into small pieces known as microplastics (MPs), which can leak some of their own additives or act as an accumulator absorbing contaminants from the medium. Most of these compounds are not yet regulated and are called contaminants of emerging concern (CECs). The accidental ingestion of plasticborne CECs by sea animals can cause ecological and toxic effects if the contaminants are assimilated by the organism and thus enter in the feed chain and finally in the human body (bioavailability, BAV). The traditional log *P* parameter does not serve to predict BAV since it only takes into account the hydrophobicity of the compound but the real interaction with the cells of living beings. In this work, we evaluate the BAV of CECs in-vitro using soybeanphosphatidylcholine-based liposomes as a biomimetic cell membrane to simulate the small intestine in which the bioaccessible compounds are predominantly absorbed and incorporated into the bloodstream. For this purpose, liposomes covalently attached onto polymeric monolithic surfaces are used to isolate bioaccessible CECs in gastrointestinal fluids in the mimicry of the human intestinal absorption via dispersive biomimetic solid phase extraction (d-BMSPE) or magnetic d-BMSPE in the case of incorporating magnetic nanoparticles. The % BAV was predicted using extraction efficiency measured by HPLC. The lipid bilayer might extract the CECs by electrostatic, polar and hydrophobic/partition interactions and thus, the proposed tool seems to be a better in-vitro resource to predict bioaccumulation than studies using merely log *P* values.

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RELIABLE PLASMONIC ELISA EXPLOITING AUTOMATIC FLOW METHODOLOGY

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Plasmonic enzyme-linked immunosorbent assays (ELISA) using metal nanoparticles (NP) is a good substitute to traditional ELISA counterparts for naked-eye detection of biomolecules and small contaminants at trace levels. However, plasmonic ELISA involving end-point detection lacks ruggedness since the generation or etching of NP is greatly dependent on every experimental parameter performed in the microplate. To avoid the above drawbacks, this communication reports on a competitive ELISA combined with the in-line generation of gold nanoparticles (AuNPs) exploiting flow analysis/flow chemistry methodology. Glucose oxidase enzyme was conjugated to a secondary antibody and yielded hydrogen peroxide that acted as the reducing agent of the Au(III)/citrate system in the flow network composed of two microsyringe pumps, a 24-position multiposition valve and a reaction coil. The localized surface plasmon resonance of AuNPs generated in-situ is real-time monitored using a USB miniaturized photometer. The determination of diclofenac in seawater without any prior sample treatment was selected as a proof-of-concept. The proposed automatic fluidic approach has a reproducible timing in AuNPs nucleation and growth along with the unsupervised absorbance detection with a dynamic range for diclofenac spanning from 0.01 to 10 µg L^{-1} and a LOD of 0.001 µg L^{-1}, that is, one order lower than that of a conventional colorimetric ELISA. Repeatability and intermediate precision were <4% and <14%, respectively, as compared to RSDs as high as 30% as obtained with the batchwise plasmonic ELISA counterpart.

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EXTRACTION OF BIOACTIVE COMPOUNDS FROM FOOD PROCESSING BY-PRODUCTS IN A BIOREFINERY CONTEXT

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Plant-based food by-products are composed mainly of organic fraction with carbohydrates, proteins, lipids that can be exploited within a biorefinery. Additionally, they contain natural bioactive molecules with great potential for the food, pharmaceutical and cosmetic sectors. The market for these natural bioactive compounds has doubled to 515 billion in the last 5 years. In this context, the aim of this study was to determine the content of major structural components, bioactive compounds profile, and the antioxidant activities of peach juice by-product (PJB) and tomato pomace (TP) derived from fruit juice concentrate production and tomato processing, respectively. Free-drying and oven-drying were applied to both materials to reduce water content to preserve them during storage. The bioactive molecules from PJB and TP were obtained by applying conventional extraction methods in a sequential manner to obtain both the extractable and non-extractable bioactive compounds. These methods were compared with an enzyme-based extraction process. In addition, the enzymatic accessibility of the carbohydrate fraction of the freeze-dried and oven dried PJB and TP was also studied using different commercial enzyme preparations. The complete evaluation of these food by-products in terms of chemical composition, bioactive profile, antioxidant capacity, and carbohydrate accessibility after different treatments is paramount to delineate integrated strategies for their industrial exploitation in a circular bioeconomy system. The development of such technologies could boost fruit and vegetable processing industries by diversifying their product supply and reducing their impact on the environment.

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STUDY OF PATCHOULI ESSENTIAL OIL CHEMICAL COMPOSITION AS A FUNCTION OF PLANT PART, ACID HYDROLYSIS AND DISTILLATION TIME

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Patchouli (*Pogostemon cablin*, Lamiaceae) essential oil (EO) is one of the most important raw materials and it has a high demand in the flavor and fragrance, food, pharmaceutic, cosmetics, and perfumery industries [1]. Patchouli EO quality is regulated by International Norm ISO 3757 (2002) [2]. In order to match the international norm, it is necessary to study chemical composition changes, which depend on the characteristics of the plant material and the distillation technique. In this work, patchouli plants were cultivated in experimetal plots, harvested and air-dried in the shade, at the CENIVAM Research Center in Bucaramanga, Colombia. The EO were obtained by microwave-assisted hydrodistillation (MWHD) and steam distillation (SD), from different plant parts (leaves, stems and their mixture), with an acid treatment, and taking oil fractions in time. The EO chemical composition was determined by GC/MS (AT GC 6890 Plus, AT MSD 5975), using the linear retention indices for each component measured on both polar and non-polar columns and by comparison of the experimental mass spectra with those from databases (Adams and NIST) and literature. The EO yields and chemical compositions showed variations according to the parameters studied. In all EO, patchoulol was the major compound (34.0-42.0%). The EO obtained only from stems was rich in pogostone (31.0%). Patchouli oil yield increased with MWHD distillation time (45-150 min). The fractions of patchouli oil obtained by SD, every 30 min, allowed to understand the extraction process of volatile secondary metabolites over time. Based on the results of the chemical composition of all EO analyzed, it was determined that the plant under study was patchoulol-chemotype, whose high content (>35%) revealed an AE of high quality and commercial value.

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EXTRACTION AND ANALYSIS BY UHPLC/ESI Q-ORBITRAP-MS OF PESTICIDE RESIDUES IN TROPICAL FRUITS

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The demand for tropical fruits with new flavors is rapidly increasing in many countries of Europe [1]. However, these products must fulfill the maximum residue limits (MRLs) of pesticides to ensure consumers safety [2]. The development of effective methods for multiresidue pesticides analysis is required in the fruit-producing countries. Our aim was to establish a method for the analysis of pesticide residues in goldenberry (*Physalis peruviana*), avocado (*Persea americana*) and gulupa (*Passiflora pinnatistipula*) using ultra-high performance liquid chromatography, coupled to electrospray Q-Orbitrap mass spectrometry (UHPLC/ESI Q-Orbitrap-MS) [3]. Sample extraction and clean-up followed the buffered QuEChERS procedure [3]. The method allowed the detection of >700 pesticides in fruit samples, of which 30 were used to evaluate recoveries, ranging from 77% to 110% at 100 μg/kg, and to construct nine-point calibration curves between 1-100 μg/L equivalent to 4-400 μg/kg. Some pesticides showed more than one adduct, namely $[M + H]^+$, $[M + NH_4]^+$, and/or $[M + Na]^+$. Screening of pesticides in samples was based both on their retention times (± 0.5 min) and on the mass accuracy (Δppm < 3) of the characteristic ions, which have the highest abundance to increase their detectability. The method proved to be sensitive enough to quantify most of the pesticides at <10 μg/kg. UHPLC/ESI Q-Orbitrap-MS along with QuEChERS sample preparation offered a practical qualitative and quantitative method for the analysis of pesticide residues in routine monitoring programs for food safety.

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OPTIMIZATION OF FLAVONOID SOLVENT EXTRACTION FROM TROPICAL FLOWERS

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Anthocyanins are flavonoids found in the grape peels, raspberries, and in *Hibiscus* rosa-*sinensis* flowers, among others. They are responsible for the typical coloration of these species [1]. The color differences depend on anthocyanin nature and their concentrations. Typically, anthocyanines are analyzed by HPLC and their identification is carried out by LC-MS [2]. In this work, the extraction of flavonoids was studied, for which a fractional experimental design with five variables was done. The variables studied were, as follows: ethanol-water ratio, temperature, extraction time, vegetal material-solvent ratio, and acid concentration. The effects of these variables on the antioxidant capacity of *Hibiscus rosa-sinensis* extracts were evaluated. The lyophilized flowers (1,0 g) were weighed, the hydroethanolic solution to be evaluated was added and the mixture was extracted in an ultrasonic bath (Elmasonic S15H, Singen, Germany), during the defined extraction times. The residue was separated by filtration (Whatman filter paper N°1) and was extracted once more. All the extracts had been stored at 7 °C, in the absence of light, before their antioxidant capacity was evaluated. For the statistical treatment of the data, the ANOVA of the results was performed. The response variable was the oxygen-radical absorption capacity, evaluated by the ORAC method; all the measurements were done in triplicate, the results were expressed as the mean value ± the standard deviation. After doing all the statistical analysis, a mathematical model with adjusted coefficient of determination was proposed ($R^2 \geq 0.98$), where the best extraction conditions were, as follows: ethanol-water ratio 52,5:47,5 (v/v), temperature 50 °C, extraction time 15 min, material-solvent ratio 1:40 (g/mL), and HCl concentration (0,5%), the ORAC value was 3510±26 µmol Trolox®/g extract. Each extract was prepared in 1 mL of acetonitrile-water mixture with formic acid (0,2%). The following major flavonoids were identified by UHPLC-ESI$^+$-Orbitrap-MS: cyanidin-3-glucoside and cyanidin-sophoroside. Other flavonoids found were quercetin-dihexoside, quercetin-glucoside and naringenin-hexuronide. It was observed that cyanidin-sophoroside was the anthocyanin common to all *Hibiscus* flowers of different colors, purple, pink, orange, or red.

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UNDERSTANDING THE COMPOSITION AND CONCENTRATION OF CUTICULAR WAXES OF *PRUNUS CERASIFERA* VAR. *PISSARDI*

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The interface between leaves and the surrounding environment is formed by the wax-covered plant cuticle, which is hydrophobic and highly impermeable to water. Its chemical characterization offers a very valuable information mainly related to the potential of urban trees to act as monitors of pollution. However, there is a lack of information of the cuticular wax composition of many of these trees.

The main goal of this work is the optimization and development of a fast and reliable method to determine 10 target fatty acids in the cuticular waxes of *Prunus cerasifera* var. *pissardi*. For sample preparation, the efficiency of two simple techniques, vortex extraction (VE) and ultrasound-assisted extraction (UAE) were assessed. Critical experimental parameters affecting extraction such as the extraction solvent and time were optimized by experimental design to obtain the highest extraction efficiency. Analytical determination was performed by gas chromatography-mass spectrometry (GC-MS). The selected conditions involved the use of UAE as extraction technique, ethyl acetate as solvent and only 2 minutes for the quantitative extraction. Under these conditions, the whole methodology was succesfully validated in terms of linearity, accuracy and precision.

Results showed long-chain saturated acids, such as stearic and palmitic, were predominant in the extracts at concentration of several hundreds of mg kg^{-1}. Besides, a screening analysis was performed to identify other chemical constituents of the cuticular waxes, revealing the presence of alcohols and aldehydes derived from fatty acids.

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EVALUATING THE PRESENCE AND CONTENTS OF PHYTOCHEMICALS IN HONEY SAMPLES: POLYPHENOLS AS INDICATORS TO IDENTIFY THEIR BOTANICAL ORIGIN

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Honey is a natural food product well known for its high nutritional value. Apart from sugars, it contains phytochemicals, a wide class of nutraceuticals found in plants, including polyphenols and flavonoids that are compounds with highly demonstrated antimicrobial and antioxidant capacities.

The main goal of this work is the development of an analytical methodology to obtain the polyphenolic profile of honeys from different varieties and pollen sources. Other indexes such as the total polyphenolic content (TPC) and antioxidant activity (AA) were also evaluated. Advanced statistical tools such as analysis of variance (ANOVA) and principal component analysis (PCA) will be employed to obtain models that allow classifying the different honeys according to their origins.

As regards sample preparation, miniaturized vortex (VE) and ultrasound (UAE) assisted extraction employing aqueous solvent were employed and TPC and AA were measured by spectrophotometric techniques. Individual quantification of the target polyphenols was carried out by liquid chromatography-tandem mass spectrometry (LC-MS/MS). Results revealed that more than 20 different polyphenols were detected in the analyzed samples, reaching up to hundreds of µg g^{-1}. ANOVA and PCA based on the results from TPC, AA and individual polyphenols determination showed that significant differences appeared depending on the honey variety, being several of the identified polyphenols responsible of the main differentiation. This study demonstrates that the combination of chromatographic analysis, mass spectrometry detection and PCA are suitable tools to investigate the botanical authentication of honey.

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DETERMINATION OF SILOXANES IN WASTEWATER SAMPLES USING MAGNETIC GRAPHENE OXIDE AS SORBENT FOR MAGNETIC DISPERSIVE SOLID-PHASE MICROEXTRACTION

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Nowadays, new requirements for analytical chemistry are growing to solve emerging problems such as global environmental concerns. To address these new challenges, the development of new and more sensitive methods to determine the pollutants is needed. The list of new pollutants or emerging pollutants has grown strongly in recent years, constituting a new source of pollution that is increasingly in the spotlight because they cause serious environmental damage despite their low concentration. Siloxanes, which are saturated chain polymers of silicon-oxygen hydrides found in a wide range of daily beauty and personal care products [1], are an example of these new pollutants. A large number of these compounds enter in the city's sewage networks. In this manner, they can reach wastewater treatment plants (WWTPs), causing severe problems for power generation systems [2]. In this work, a developed method based on magnetic dispersive solid-phase microextraction [3] has been applied for the simultaneous determination of different siloxanes in wastewater samples from Portuguese WWTPs. The obtained results revealed the prevalence of siloxane D5, following the same trend as in the literature [4]. We also noticed that during the summer, when coastal areas have a higher population, the concentration of siloxanes in these wastewater collectors rises. In the winter, however, the concentration drops in these coastal areas, and siloxanes have been increased in the collector of urban areas. Based on these results, it is easy to conclude that the siloxanes concentration is strongly related to human activities.

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DATE-RAPE EVIDENCE THROUGH FAST DETERMINATION OF γ-BUTYROLACTONE IN ADULTERATED BEVERAGES

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An infrared spectroscopy (IR) based methodology has been developed to determine γ-butyrolactone (GBL) in adulterated beverages. The proposed method allows the direct screening of GBL in beverages and involves a minimum sample treatment requiring less than 2 min for quantitative determination of GBL. Sensitivity of IR method was improved by using liquid-liquid extraction (LLE) providing detection limits of 0.023 mg g^{-1}. Accuracy of the proposed methodology was evaluated through the analysis of soft beverages and alcoholic cocktails spiked with GBL at concentration levels ranging from 0.075 to 10 mg g^{-1} providing recovery values from 91 to 100%. GBL was determined in twelve blind-spiked beverages, including from mineral water to wine and cocktails. Results obtained were statistically comparable to those provided by a liquid chromatography (LC) reference methodology and consistent with the spiked values. As compared with the analytical features of methods available in the literature to determine GBL in beverages, the use of the proposed methodology provides a higher linear range than HPLC-UV/Vis and HPLC-MS/MS [1]. However, the LoD was 15 times higher than that obtained by chromatography using MS/MS detection. On comparing with the actual features of the system used as reference procedure, the previous extraction of GBL improves the LoD by a factor of 3.7. Furthermore, the use of a low volume transmission cell allows decreasing the sample and the extractant volumes, allowing repeated measurements and greening the methodology by scale reduction. Therefore, the use of LLE-FTIR allowed a simple, sensitive and quantitative determination of GBL in soft beverages and alcoholic cocktails, thus evidencing its use for sex submission intention, without the requirements of sophisticated instrumentation.

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COMPLETE SOLUTION TO ANALYZE SVOCS IN WATER BY GC-APCI-QTOF HIGH RESOLUTION MS SYSTEM

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This work describes the use of the Bruker µDROP method for sample preparation, followed by GC-APCI-QTOF high resolution system for the analysis of semi-volatiles compounds (SVOCs) in various control and natural (crude) water matrices.

Bruker µDROP is a proprietary, miniaturized, and ultra-sensitive method for the analysis of water samples. This technique and its successful application to water sample analysis have been previously described using traditional GC-MS/MS Triple quads instruments.

Using Bruker's GC-APCI-QTOF systems, there is no practical limit to the number of targets that may be sought and identified. This detection capability, with demonstrated high resolution and high sensitivity, has established QTOF MS as a highly valuable analytical tool for both targeted and untargeted screening approaches fulfilling the most stringent analytical regulations to analyze pollutants in water matrices.

DETERMINATION OF HORMONES IN WATER BY LIQUID BACK EXTRACTION OF TF-SPME-SBSE AND LC-MS/MS

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Laboratory samples are typically extracted prior to analysis by sensitive GC-MS or LC-MS/MS methods to separate the analytes of interest from the bulk of matrix components that could interfere with the analysis. Typical extraction methods include liquid-liquid extraction or solid phase extraction strategies; however, these can involve the use of large volumes of hazardous chemicals and may require the evaporation of solvents to concentrate the final extract and/or exchange the solvent system to one more amenable to the analytical technique being used. Extraction techniques that avoid hazardous chemicals while still being able to concentrate and separate the analytes of interest would be of great benefit to those analytical laboratories hoping to achieve safer and less labor intensive methods of preparing samples for analysis. In this study, Thin Film Solid Phase Micro-Extraction (TF-SPME) devices with hydrophilic lipophilic balanced/polydimethylsiloxane (HLB/PDMS) coatings were investigated for their usefulness with LC-MS/MS analysis in combination with Stir Bar Sorptive Extraction (SBSE) using the GERSTEL Twister®. The Twister is used both to stir the sample and to provide additional PDMS phase volume resulting in enhanced overall extraction efficiency as previously reported[1,2]. Six hormone compounds were extracted from water using TF-SPME-SBSE and then back-extracted from the devices using methanol. The GERSTEL MPS was used to inject the extracts into an LC-MS/MS system for subsequent analysis.

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COMPARISON OF THREE TYPES OF THIN FILM-SOLID PHASE MICROEXTRACTION PHASES FOR BEVERAGE EXTRACTIONS

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Thin Film Solid Phase Micro-Extraction (TF-SPME) devices with carboxen/polydimethylsiloxane (CAR/PDMS), divinylbenzene/polydimethylsiloxane (DVB/PDMS), and hydrophilic lipophilic balanced/polydimethylsiloxane (HLB/PDMS) coatings are investigated for their usefulness for beverage analysis in combination with Stir Bar Sorptive Extraction (SBSE) using the GERSTEL Twister. The Twister is used both to stir the sample and to provide additional PDMS phase volume resulting in enhanced overall extraction efficiency as previously reported[1,2]. The TF-SPME and SBSE devices are desorbed together by Thermal Desorption resulting in one combined GC/MS run. A variety of beverages are analyzed including almond milk, black tea, strawberry banana juice, amber lager, and pumpkin ale. The GERSTEL MPS is used in combination with a CIS 4 inlet and thermal desorber for automated thermal desorption of the TF-SPME devices.

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AUTOMATED EXTRACTION OF GLYPHOSATE/AMPA/GLUFOSINATE IN RED WINE PRIOR TO LC-MS/MS ANALYSIS WITHOUT DERIVATIZATION

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Since 1970, glyphosate has been used as a systemic, non-selective herbicide and crop desiccant on farms, in fields, and in public and residential areas. It is one of the most widely used herbicides worldwide.

Microbial action rapidly decomposes glyphosate into aminomethyl phosphonic acid (AMPA).

Glufosinate, another common phospho-herbicide, is structurally and functionally similar to AMPA and glyphosate, and the three molecules are often analyzed simultaneously.

Due to its relative stability in soils and sediments, and its high solubility in water, glyphosate and its principal decomposition product, AMPA, are present at low concentrations in environmental matrices and across the food chain.

The high polarity of these three molecules makes analysis difficult and typically requires a derivatization step with fluorenylmethyloxycarbonyl chloride (FMOC-Cl) to enable detection and quantitation.

The AFFINIMIP SPE Glyphosate protocol has been automated on the Gilson ASPEC 241 Liquid Handler for the enrichment and cleanup of glyphosate, AMPA, and glufosinate from red wine. LC-MS/MS analysis demonstrate high selectivity and excellent recoveries of the three compounds (from 70% to 96%).

This automated solution does not require time-consuming derivatization which introduced variability, especially in complex matrices.

MALDI-TOF MS-BASED UNTARGETED MASS FINGERPRINT PATTERN OF THE PROTEOMIC FRACTION OF FISH MUCUS AS A POWERFUL TOOL FOR ITS TRACEABILITY

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Food fraud constitute a global concern not only at economic level but can also have severe adverse health, societal and sustainability effects. Even though considered illegal and several regulatory guidelines are in practice to enforce food protection, is still a recurrent action towards the increase of financial profits, in violation of legal rules. Therefore, the development of appropriate analytical approaches to be used against food fraud is of utmost importance. In this study we explore, for the first time, the possibility of differentiation between Sparus aurata from two different mariculture farms located in Madeira island (Caniçal and Ribeira Brava), using the proteomic mass fingerprint pattern of fish mucus obtained by MALDI-TOF MS. The data were analyzed using Mass-UP software for multivariate statistical analysis and biomarker identification. It was possible to establish from the mucus protein fraction, a set of potential biomarkers for each location in a total of 35 protein fragments, being 17 specific to Caniçal located farm and 18 to Ribeira Brava farm. In addition, the mass-fingerprint approach allowed to differentiate between samples with different residence times in the sea cages, confirming the alterations that fish mucus undergoes from the moment of arrival to the moment of capture. The proposed analytical approach revealed a useful strategy providing accurate and fast results for fish geographical origin discrimination and therefore for its traceability.

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DETERMINATION OF MULTICLASS VETERINARY DRUG RESIDUES IN PORK WITH CAPTIVA EMR-LIPID CLEANUP AND LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY

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Captiva EMR–Lipid provides highly selective and efficient lipid/matrix removal without unwanted analyte loss. The novel EMR-Lipid technology removes lipids based on a combination of size exclusion and hydrophobic interaction. Effective lipid removal assures minimal ion suppression of target analytes, which significantly improves method reliability and ruggedness. The 96-well plate and 1 mL cartridge formats contain a solvent retention frit, which allows solvent-first in-well protein precipitation which streamlines sample preparation. The improved filter design gives easy flow with vacuum or positive pressure. The 3 and 6 mL cartridge formats allow gravity flow with the absence of solvent retention frits and are easy to use. Veterinary drugs have been used widely in veterinary practice to treat and prevent disease, or to enhance growth and feed efficiency. If these drugs are not administered correctly, it can lead to the presence of veterinary drug residues in foods of animal origin for human consumption, which can pose a health risk. To better control the use of veterinary drugs and protect public health, the residue levels of these drugs in meat or other foods are regulated by federal regulatory agencies. Currently the published veterinary drug residues analysis standard methods focus on only one chemical class or several chemical classes of drugs. It can take days to finishing testing and get the reports. The work flow is not only time-consuming, labor-intensive, and costly, but is also inefficient when dealing with a large number of samples. Animal tissues sample contain high amounts of proteins and lipids, and pose significant challenges with regards to sample preparation. In this study, acidified acetonitrile (5% formic acid) was used as an extraction solvent capable of efficient protein precipitation to extract analytes into the organic phase. Agilent Captiva EMR-Lipid was used for cleanup to remove lipids.

A rapid, reliable, and robust method using acidified acetonitrile extraction followed by Agilent Captiva EMR—Lipid cleanup was optimized and validated for the analysis of veterinary drug multiresidues in pork. Matrix effects were compared with and without cleanup. Results demonstrate that the optimized Captiva EMR—Lipid method provided superior matrix cleanup, and excellent recovery and precision for this type of application. This application demonstrates that selective matrix removal using Captiva EMR—Lipid provides significant advantages for complex samples such as pork, in the form of cleaner samples and higher recoveries and precision for multiresidue veterinary drug analysis.