ExTech 2023 enerife

25th International Symposium on Advances in Extraction Technologies

18th to 21st of July 2023

BOOK OF ABSTRACTS

CONTENT

WELCOME TO EXTECH 2023

We truly welcome you to the 25th International Symposium on Advances in Extraction Technologies (ExTech). It is certainly our honor to chair the 25th edition this July 2023 in Tenerife (Canary Islands, Spain).

As it is internationally recognized, the ExTech conference was first started by Prof. Janusz Pawliszyn, Honorary Chair of this edition of the symposium. In this long journey of 25 years, the ExTech Conference has taken place in different locations around the world, including: Waterloo, Canada (1999-2000), Barcelona, Spain (2001); Paris, France (2002); Florida, USA (2003); Leipzig, Germany (2004); Campinas, Brazil (2005); York, UK (2006); Ålesund, Norway (2007); Bruges, Belgium (2008); South Dakota, USA (2009); Poznan, Poland (2010); Kuala Lumpur, Malaysia (2011); Messina, Italy (2012); Joao Pessoa, Brazil (2013); Chania, Greece (2014); Guangzhou, China (2015); Toruń, Poland (2016), Santiago de Compostela, Spain (2017), Iowa, USA (2018); Guangzhou, China (2019); postponed in Colombia due to Covid (2020); Alicante, Spain (2021) and Iquique, Chile (2022), thus showing the high interest and impact of this Symposium.

ExTech is undoubtedly the most important event series in the growing fields of sample preparation, extraction technologies, and sample clean-up techniques. This forum of outstanding researchers is unique in terms of presentation of top investigations in the analytical sample preparation field, with highlights in microextraction, development of novel materials, complex analytical applications, and sustainability, while being an excellent platform for young researchers, interacting simultaneously with leading scientists from around the world. In this way, the ExTech Symposium puts in value the research presented by young scientists, with important recognitions in terms of awards for both poster and oral presentations.

We are honored to count with several loyal sponsors who have contributed to make ExTech 2023 a successful conference and which include Milestone, Markes International, and Merck as Gold Sponsors, Bruker and Gilson as Silver Sponsors, and many other such as Campus de Excelencia Internacional-ULL, Vicerrectorado de Investigación-ULL, Elsevier, Avantor, Canary Island Car Cicar, and Dermatén Clínicas together with media partners like Analytica Chimica Acta, Green Analytical Chemistry, Advances in Sample Preparation, Analytical and Bioanalytical Chemistry and LC-GC. We would also like to thank different societies which have collaborated by sponsoring grants and awards for students: the Royal Spanish Society of Chemistry (RSEQ), the Spanish Society of Chromatography and Related Techniques (SECyTA), the Spanish Society of Analytical Chemistry (SEQA), the Spanish Society of Mass Spectrometry (SEEM) and the European Chemical Society (EuChemS)-DAC Sample Preparation Study Group.

This 25th edition of the conference includes attendees from Europe, Asia and America. A total of 3 plenary lectures, 20 keynote lectures, 62 oral communications and 174 posters will be presented, half of them belonging to young scientists. This edition of the symposium will also include a panel discussion of an emerging topic: Green analytical chemistry, green sample preparation and metrics.

On behalf of the Organizing Committee, we welcome you to Tenerife and we wish you a very successful, pleasant, and productive conference and, of course, an unforgettable 25th edition!!

Verónica Pino

Chair of ExTech 2023

Javier Hernández-Borges

Chair of ExTech 2023

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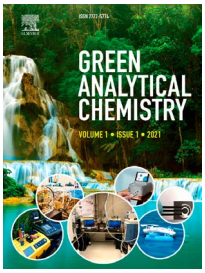

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Real Sociedad Española de Química

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SOCIEDAD ESPAÑOLA DE CROMATOGRAFÍA Y TÉCNICAS AFINES

SEEM

SamplePrep
EuChemS

SEQA
Sociedad Española de Química Analítica

EuChemS
European Chemical Society

GENERAL INFORMATION

Conference Address

Pirámide de Arona Conference Center
Avenida las Américas, s/n
38650 Playa de las Américas, Tenerife (España)
Tel: +34 922 757 545

Conference Language

The official language of the meeting is English.

Symposium Registration Desk

The registration desk is located in the Main Hall and will be open at the following times:

Tuesday, 18th July 2023	16:00 – 19:00 h
Wednesday, 19th July 2023	8:00 – 13:30 h and 15:00 – 18:00 h
Thursday, 20th July 2023	9:00 – 13:30 h and 15:00 – 18:00 h
Friday, 21st July 2023	9:00 – 13:30 h

Identification Badges

The Organizing Committee requests everybody to wear their identification badges always at the Congress to get admittance to scientific and social activities.

Book of Abstracts

The Book of Abstracts is available on the official ExTech 2023 website. You can also access it through this QR code.

Exhibition

Sponsors' exhibits are located in the Espejos Room. Exhibition hours:

Wednesday, 19th July 2023	11:00 – 12:00 h and 15:00 – 15:45 h
Thursday, 20th July 2023	11:00 – 12:00 h and 15:00 – 15:45 h
Friday, 21st July 2023	11:00 – 12:00 h

Poster Sessions

Posters set-up will take place based on the assigned poster sessions:

- **Poster Session 1 (PS1):** Tuesday, 18th July, from 16:00 h onwards, or Wednesday, 19th July, from 8:00 h to 9:00 h.
- **Poster Session 2 (PS2):** Thursday, 20th July from 8:00 h to 9:00 h.

Any supplies that might be needed to put up the poster (i.e., thumbtacks, tape, scissors, etc.) will be available on-site.

Each poster board will already have the poster code at the top. Check the code assigned to your communication in the symposium program before placing the poster.

During the Symposium, posters will be posted and available in the conference center for all attendees to peruse at any time. Each person or working group must be in attendance at their poster board on the day of their poster session:

Wednesday, 19th July 2023	**PS1**	P-01 to P-44 and YP-01 to YP-41
Thursday, 20th July 2023	**PS2**	P-45 to P-81 and YP-42 to YP-93

Do not remove your poster until the end of the assigned poster session. Poster teardown will take place as follow:

- **PS1**: Posters should be removed on Wednesday evening after 18:00 h. Any poster remaining after 18:30 h will be discarded.
- **PS2**: Posters should be removed on Thursday evening after 18:00 h. Any poster remaining after 18:30 h will be discarded.

Welcome Reception

The Welcome Cocktail will be held at the Swimming Pool Terrace of Cleopatra Hotel on Tuesday, 18th July, at 19:20 h.

Symposium Lunch

The Presymposium Course Lunch and Symposium Lunches will take place at Cleopatra Restaurant from 13:30 h to 15:00 h.

Gala Dinner

The Gala Dinner will be held at the Swimming Pool Terrace of Cleopatra Hotel on Thursday, 20th July, at 20:15 h.

Tourist Visit

The trip to El Teide National Park will be held on Friday, 21st July, at 15:00 h.

Buses will be outside Conference Center.

More information will be shared in the days leading up to and during the conference.

Wi-Fi Connection

Free access to the venue's Wi-Fi connection will be available throughout the event. Please note that you may experience a loss of connection efficiency as it is freely available to all attendees.

Network: WIFIMNR
Password: Exwimnr2015

SPONSORS' TALKS

Thursday, 20th July 9:20 h – Atenas Room

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MILESTONE HELPING CHEMISTS

Microwave-assisted sample preparation in food analysis: A highly valuable ally

Giorgia Purcaro

Thursday, 20th July 9:50 h – Auditorium Room

SILVER SPONSOR

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Chromatography free screening and quantitation enabled through SPME DART-MS

Pedro Cano

Thursday, 20th July 16:35 h – Atenas Room

GOLD SPONSOR

MERCK

33 years of SPME – A review from manufacturer's perspective

Frank Michel

Friday, 21st July 10:05 h – Auditorium Room

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MARKES international

Untargeted analysis of dairy products using vacuum-assisted techniques coupled with gas chromatography – mass spectrometry (GC–MS)

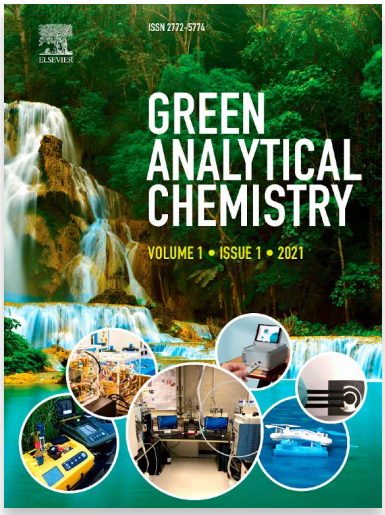
Rachael Szafnauer

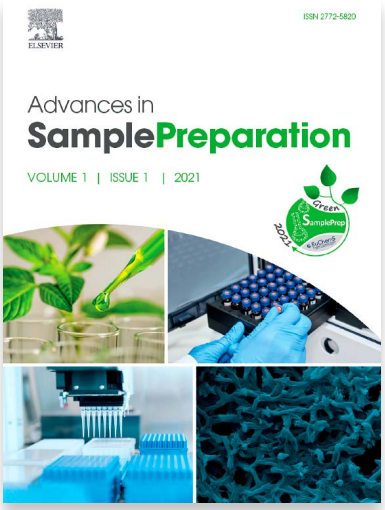
JOURNAL SPECIAL ISSUES

Analytica Chimica Acta, Green Analytical Chemistry, and Advances in Sample Preparation (Elsevier) will be publishing a joint Virtual Special Issue (VSI) for the 25th International Symposium on Advances in Extraction Technologies.

This VSI intends to cover the most exciting publications of research presented at the conference.

Manuscript submission deadline: 1st February 2024.





Keywords: Sample preparation, microextraction, green analytical chemistry, sustainability, complex samples, novel materials.

To ensure that all manuscripts are included into the VSI, it is important to select **"VSI: ExTech 2023"** as article type during the submission process.

Manuscripts submitted in **Gold OA journals** (Green Analytical Chemistry and Advances in Sample Preparation) will be subjected to a **full fee waiver** for being published in this VSI.

Guest Editors:

Prof. Verónica Pino	**Prof. Javier Hernández-Borges**
Dr. María J. Trujillo-Rodríguez	**Dr. Javier González-Sálamo**

For any inquiries about the appropriateness of contribution topics, please contact Prof. Verónica Pino via email at veropino@ull.edu.es

Manuscripts must be submitted electronically via the Elsevier Editorial Manager site for the journals. Guidance on how to prepare the manuscript can be found in each journal website. Submissions are accepted any time before the deadline.

Supel™ BioSPME Device

New sample preparation for clinically relevant analytes and correlation to externally validated methods.

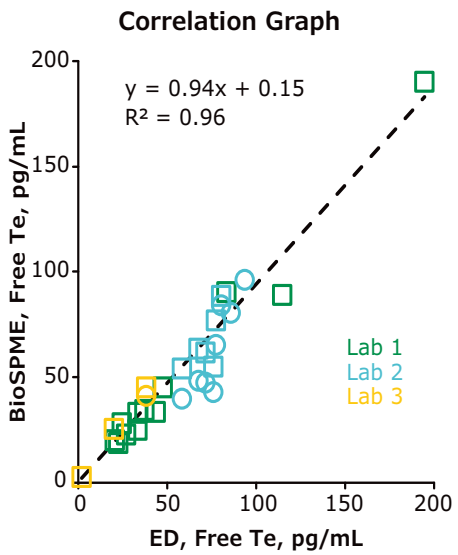
Method available as either automated or manual

Sample Preparation	Supel™ BioSPME	Equilibrium Dialysis
Time (hour)	~1 hour	6-24 hours

Steps Involved:

1. Condition
2. Wash
3. Extraction⁺
4. Wash
5. Desorb and Derivatize*
6. Analyze

⁺heated shaker req. *if necessary



Application: Free testosterone

- 200 µL of serum/sample
- extracted calibration curve
- C18 coated pin for microextraction
- comparison with 3 independently validated ED sample prep

Reproducibility across concentrations

Free Te, pg/mL	RSD's	Replicates
28.2	3.0	3
47.1	10.7	4
77.0	7.5	3
190.3	8.0	3

Be on the look-out for upcoming free hormone applications: triiodothyronine (T3), thyroxine (T4), and estradiol (E2).

Supel™ BioSPME devices are to be used for sample preparation of serum and plasma for the subsequent analysis and concentration determination of free analytes via LC/MS and LC/MS/MS. The Supel™ BioSPME devices are to be used with compatible automation instruments via gripper paddle maneuver, or manually via hand maneuver through the sample preparation workflow steps. Supel™ BioSPME devices are "For R&D use only. Not for drug, household, or other uses."

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PRESYMPOSIUM COURSE

"Solid-Phase Microextraction – Insights, Present and Future"

The short courses will be taught on July 18th, from 9:00 h to 17:30 h in the Atenas Room.

Coordinator: Dr. Rafael Lucena

1st Session

9:00 – 11:00 **SPME fundamentals and applications**

Janusz Pawliszyn
University of Waterloo, Canada

11:00 - 11:30 **Coffee Break (Hall 2)**

2nd Session

11:30 – 13:30 **Direct SPME-MS**

Wei Zhou
University of Waterloo, Canada

13:30 - 15:00 **Lunch Break (Cleopatra Restaurant)**

3rd Session

15:00 – 16:30 **Strategies of using microextraction in clinical and biomedical research**

Barbara Bojko
Nicolaus Copernicus University in Torun, Poland

4th Session

16:30 – 17:30 **On-site extraction**

Rafael Lucena
University of Córdoba, Spain

Tuesday 18th July		Wednesday 19th July		Thursday 20th July		Friday 21st July	
	8:00	Registration					
9:00	9:00	Keynote Auditorium	Keynote Atenas	9:00 Keynote Auditorium	Keynote Atenas	9:00 Keynote Auditorium	Keynote Atenas
Short course on micro-extraction	9:20	Orals session 1 Auditorium	Orals session 2 Atenas	9:20 Orals session 3 Auditorium	Orals session 4 Atenas	9:20 Orals session 7 Auditorium	Orals session 8 Atenas
				10:20 Keynote Auditorium	Keynote Atenas		
	10:40	Keynote Auditorium	Keynote Atenas	10:40 Keynote Auditorium	Keynote Atenas	10:40 Keynote Auditorium	Keynote Atenas
11:00 Course coffee break	11:00	Coffee break, exhibition and poster session 1		11:00 Coffee break, exhibition and poster session 2		11:00 Coffee break and exhibition	
11:30 Short course on microextraction	12:00	Keynote Auditorium	Keynote Atenas	12:00 Plenary Lecture		12:00 Closing Plenary Lecture	
	12:20	Young Orals session 1 Auditorium	Young Orals session 2 Atenas	12:40 Young Orals session 5 Auditorium	Young Orals session 6 Atenas	12:40 Presentation of ExTech2024 - Closing Ceremony and Awards	
13:30 Course lunch	13:30	Symposium lunch		13:30 Symposium lunch		13:30 Symposium cold lunch	
15:00 Short course on micro-extraction	15:00	Exhibition and poster session 1		15:00 Exhibition and poster session 2		15:00 Trip to El Teide National Park	
	15:45	Discussion Table – Green Metrics		15:45 Keynote Auditorium	Keynote Atenas		
16:00 Registration				16:05 Orals session 5 Auditorium	Orals session 6 Atenas		
	16:35	Keynote Auditorium	Keynote Atenas				
	16:55	Young Orals session 3 Auditorium	Young Orals session 4 Atenas	17:10 Young Orals session 7 Auditorium	Young Orals session 8 Atenas		
17:25 Registration	18:00			18:00			
18:00 Opening Ceremony							
18:20 Opening Plenary Lecture							
19:20 Welcome cocktail							
				20:15 Gala dinner			

SYMPOSIUM PROGRAM

Tuesday, 18th July 2023

Auditorium

18:00 **Opening Ceremony**

Rosa Dávila – President
Island Council of Tenerife (Spain)
Francisco J. García Rodríguez – Rector
University of La Laguna (Spain)
Verónica Pino – Chairwoman
University of La Laguna (Spain)
Javier Hernández-Borges – Chairman
University of La Laguna (Spain)
Janusz Pawliszyn – Honorary Chairman
University of Waterloo (Canada)

18:20 **Opening Plenary Lecture**

Opening Plenary Session
Chairs: Rafael Lucena[1] and Emanuela Gionfriddo[2]
[1]University of Córdoba (Spain), [2]University of Toledo (USA)

PL-01 Think big but design small and efficient, a green path of microextractions

Stig Pedersen-Bjergaard and Janusz Pawliszyn

19:20 **Welcome Reception (Cleopatra Swimming Pool Terrace)**

Wednesday, 19th July 2023

Auditorium

Oral Session 1: New Extraction Materials
Chairs: Manuel Miró[1] and María José Ruiz-Ángel[2]
[1]University of the Balearic Islands (Spain), [2]University of Valencia (Spain)

9:00 **Keynote Lecture**

KN-01 Smart materials and low-cost supports: A well-matched couple for sample preparation

José Manuel Herrero-Martínez, Héctor Martínez-Pérez-Cejuela, María Vergara-Barberán, Enrique Javier Carrasco-Correa, Miriam Beneito-Cambra, María Jesús Lerma-García, and Ernesto Francisco Simó-Alfonso

9:20 **Oral Communications**

9:20 **O-01 Selective extraction of high-purity lignin from biomass with ternary deep eutectic solvents**

Liang Ying Ee, Yong Kuok Tan, Jiapei Miao, Hui Ting Chu, and Sam F.Y. Li

9:35 **O-02 Adsorbent-assisted supercritical fluid extraction: A green process for the recovery of terpenoids with neuroprotective potential from olive oil agro-industrial waste**

Zully Jimena Suárez-Montenegro, Gerardo Álvarez-Rivera, José Mendiola, Elena Ibáñez, and Alejandro Cifuentes

9:50 **O-03 Multiwalled carbon nanotubes embedded in a polymeric matrix as a new material for thin-film microextraction (TFME) of pesticides under different configurations: Suspended film and pipette tip**

Ivonne Quintanilla, Clàudia Fontàs, and Enriqueta Anticó

10:05 **O-04 A hydrophobic eutectic mixture as sustainable extraction solvent in LC-MS food analyses**

Chiara Dal Bosco and Alessandra Gentili

10:40 **Keynote Lecture**

KN-02 New miniaturized approaches for the analysis of low-availability samples

Alberto Chisvert, Juan L. Benedé, José Grau, Víctor Vállez-Gomis, Cristian Azorín, and Guillem Peris-Pastor

Atenas Room

Oral Session 2: Novel Sorbents and Solid-Phase Extraction Configurations
Chairs: Valérie Pichon[1] and María Ramos-Payán[2]
[1]Sorbonne University (France), [2]University of Sevilla (Spain)

9:00 **Keynote Lecture**

KN-03 Synthesis of novel hybrid nanocomposites based on clay coated by physical vapor deposition for solid-phase microextraction of emergent pollutants from aqueous samples

Juliana Rincón-López, Álvaro Pulzara-Mora, and Milton Rosero-Moreano

9:20 **Oral Communications**

9:20 **O-05 New trends in sample preparation using 3D-printed devices**

Enrique Javier Carrasco-Correa, Miriam Beneito-Cambra, María Jesús Lerma-García, Ernesto Francisco Simó-Alfonso, José Manuel Herrero-Martínez, and Manuel Miró

9:35 **O-06 Valve for flexible in-time SPE prior HPLC**

David J. Cocovi-Solberg, Stephan Schnidrig, Manuel Miró, and Stephan Hann

9:50 **O-07 Carbon nanotubes-based membranes for disk solid-phase extraction**

Alessandra Gentili

10:05 **O-08 Accurate and sensitive analysis of protein biomarkers at the intact and peptide map level by on-line aptamer affinity solid-phase extraction capillary electrophoresis-mass spectrometry**

Hiba Salim, María Vergara-Barberán, Laura Pont, Estela Giménez, Victoria Sanz-Nebot, and Fernando Benavente

10:20 **O-09 NH_3^+ modified SPIONs based extraction material for methotrexate study in pharmaceuticals nanodelivery systems**

Yolanda Moliner-Martínez, Emanuel Marano, and Pilar Campins-Falcó

10:40 **Keynote Lecture**

KN-04 Sustainable miniaturized sample preparation strategies to assess the global impact of recycled tire crumb rubber microplastics

María Llompart, Andrés Duque, Sergio Sóñora, Daniel Armada, Antía Martínez, Pablo García, María Celeiro, and Thierry Dagnac

11:00 **Coffee Break. Sponsors Exhibition. Poster Session 1 (Espejos Room)**

Auditorium

Young Oral Session 1

Chairs: Jorge Pasán[1] and Juan L. Benedé[2]

[1]University of La Laguna (Spain), [2]University of Valencia (Spain)

12:00 **Keynote Lecture**

KN-05 On-site environmental extraction devices based on open-source technologies

Francisco Antonio Casado-Carmona, Soledad Cárdenas, and Rafael Lucena

12:20 **Young Oral Communications**

12:20 **YO-01 Metal-organic frameworks-coated glass vials for analytical microextraction**

Iván Taima-Mancera, María J. Trujillo-Rodríguez, Juan H. Ayala, Jorge Pasán, and Verónica Pino

12:35 **YO-02 Miniaturized magnetic-pipette tip microextraction: A new tool for microsample analysis**

José Grau, María Moreno-Guzmán, Luis Arruza, Miguel Ángel López, Alberto Escarpa, and Alberto Chisvert

12:50 **YO-03 Sustainable gelatin-coated papers for the determination of steroid hormones in waters**

Teerayanee Chaipet, Beatriz Fresco-Cala, Chongdee Thammakhet-Buranachai, Rafael Lucena, and Soledad Cárdenas

Atenas Room

Young Oral Session 2

Chairs: Antonio Martín-Esteban[1] and Idaira Pacheco-Fernández[2]

[1]Spanish National Research Council (Spain), [2]Kyoto University (Japan)

12:00 **Keynote Lecture**

KN-06 Harnessing microextraction methodologies for the characterization of complex samples

Emanuela Gionfriddo

12:20 **Young Oral Communications**

12:20 **YO-04 Ionic liquids and surfactants as coating materials for iron oxide-based magnetic sorbents applied in the extraction of pharmaceuticals from biological samples**

Natalia Treder, Ilona Olędzka, Anna Roszkowska, Tomasz Bączek, and Alina Plenis

12:35 **YO-05 Synthesis and characterization of polystyrene-based sorbents for microextraction of selected psychoactive drugs from biological samples**

Paweł Stelmaszczyk, Mateusz Iwan, Dominika Pawcenis, and Renata Wietecha-Posłuszny

12:50 **YO-06 Headspace solid-phase microextraction as high throughput technique to extract potential urinary prostate cancer biomarkers. A metabolomic approach**

Giulia Riccio, Cristina V. Berenguer, Ferdinando Pereira, Pedro Berenguer, Cristina P. Ornelas, Ana Célia Sousa, João Aragão Vital, Maria do Carmo Pinto, Jorge A.M. Pereira, Viviana Greco, and José S. Câmara

13:30 **Symposium Lunch (Cleopatra Restaurant)**

15:00 **Sponsors Exhibition. Poster Session 1 (Espejos Room)**

Auditorium

Discussion Table on Green Metrics
Moderator: Renata Wietecha-Posłuszny
Jagiellonian University (Poland)

15:45 **Green Metrics Table**

Marek Tobiszewski, Yolanda Moliner-Martínez, Torsten C. Schmidt, and Frank Michel

Auditorium

Young Oral Session 3
Chairs: Ana M. García-Campaña[1] and Javier González-Sálamo[2]
[1]University of Granada (Spain), [2]University of La Laguna (Spain)

16:35 **Keynote Lecture**

KN-07 Omics analysis of natural products is going greener: Opportunities from new materials combined with microextraction techniques

Cecilia Cagliero, Giulia Mastellone, Gaia Bechis, Arianna Marengo, Barbara Sgorbini, and Patrizia Rubiolo

16:55 **Young Oral Communications**

16:55 **YO-07 Miniaturized QuEChERS combined with HPLC-MS/MS for determination of atropine and scopolamine in leafy vegetables**

Lorena González-Gómez, Sonia Morante-Zarcero, Jorge A.M. Pereira, José S. Câmara, and Isabel Sierra

17:10 **YO-08 A new microwave-assisted extraction technology for the profiling of free and esterified fatty acid in food matrices**

Donatella Ferrara, Angelica Fina, Chiara Cordero, and Giorgia Purcaro

17:25 **YO-09 Ultra-high pressure supercritical fluid extraction (SFE) to obtain a terpenoids-purified microalgae extract at semi-pilot scale**

Víctor M. Amador-Luna, Lidia Montero, José A. Mendiola, Alejandro Cifuentes, Elena Ibáñez, and Miguel Herrero

17:40 **YO-10 Fiber-type *Cannabis sativa* L.: Innovative extraction methods for the analysis of the non-volatile fraction**

Giulia Mastellone, Gaia Bechis, Arianna Marengo, Barbara Sgorbini, Patrizia Rubiolo, Verónica Pino, Jared L. Anderson, and Cecilia Cagliero

17:55 **YO-11 Towards high throughput analysis using 96-well plate SPE for residue monitoring in food control**

Ane Arrizabalaga-Larrañaga, Dieke van Doorn, and Saskia S. Sterk

Atenas Room

Young Oral Session 4

Chairs: Stig Pedersen-Bjergaard[1] and Guillermo Lasarte-Aragonés[2]

[1]University of Oslo (Norway), [2]University of Córdoba (Spain)

16:35 **Keynote Lecture**

KN-08 Aptamer-based sorbents for the selective extraction of molecules and ions at trace levels in complex samples

Fanny Gignac, Audrey Combès, Nathalie Delaunay, and Valérie Pichon

16:55 **Young Oral Communications**

16:55 **YO-12 A green ionic liquid-based three-phase partitioning system as a simple miniaturized platform for the analysis of human saliva**

Raúl González-Martín, María J. Trujillo-Rodríguez, Francisca A. e Silva, Jacob Lorenzo-Morales, Mara G. Freire, and Verónica Pino

17:10 **YO-13 A magnetic deep eutectic solvent for dispersive liquid-liquid microextraction of bisphenols from food samples**

Cristina Zapater, Miguel Ángel Aguirre, Lorena Vidal, and Antonio Canals

17:25 **YO-14 Use of aqueous biphasic systems to improve the analysis of cancer biomarkers**

Francisca A. e Silva, Maria S.M. Mendes, Marguerita E. Rosa, João A.P. Coutinho, João P. Conde, and Mara G. Freire

17:40 **YO-15 Evaluating new generations of magnetic ionic liquids as extraction platforms for organic compounds present in biological fluids**

María J. Trujillo-Rodríguez, Sirintorn Jullakan, Raúl González-Martín, Nabeel M. Abbasi, Shashini De Silva, Jared L. Anderson, and Verónica Pino

Thursday, 20th July 2023

Auditorium

Oral Session 3: Analysis of Complex Samples

Chairs: María Llompart[1] and Milton Rosero-Moreano[2]

[1]University of Santiago de Compostela (Spain), [2]University of Caldas (Colombia)

9:00 **Keynote Lecture**

KN-09 Vacuum-assisted headspace microextraction: From theory to a new product

Elefteria Psillakis

9:20 **Oral Communications**

9:20 **O-10 Autonomous dried blood spot analysis by capillary electrophoresis**

Pavel Kubáň, Miloš Dvořák, Lenka Ryšavá, and Ondrej Moravčík

9:35 **O-11 Extraction of β-blockers from urine with a polymeric monolith modified with imidazolium ionic liquids in spin columns and paper**

María José Ruiz-Ángel, Óscar Mompó-Roselló, Jaume Agustí-Arcón, Ernesto Francisco Simó-Alfonso, María Celia García-Álvarez-Coque, and José Manuel Herrero-Martínez

9:50 **O-12 Chromatography free screening and quantitation enabled through SPME DART-MS**

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Miguel Ángel Pérez, William Fatigante, Brian D. Musselmann, Elena Bueno, and Pedro Cano

10:05 **O-13 Sample preparation strategies followed by GC×GC based techniques for lipids investigation**

Marco Beccaria, Angelica Fina, Marco Piparo, Pierre Giusti, Pierre-Hugues Stefanuto, Giorgia Purcaro, and Jean-François Focant

10:20 **Keynote Lecture**

KN-10 Automation of sample treatment based on flow techniques for pharmaceutical development

Marcela A. Segundo, Diana R. Cunha, M. Beatriz Quinaz, Luisa Barreiros, and Sara S. Marques

10:40 **Keynote Lecture**

KN-11 Transition metal oxide-based sol-gel media for capillary microextraction

Abdul Malik, Sheshanka Kesani, and Minh Phuong Tran

Atenas Room

Oral Session 4: Environmental Analysis

Chairs: Yolanda Moliner-Martínez[1] and Pablo Richter[2]

[1]University of Valencia (Spain), [2]University of Chile (Chile)

9:00 **Keynote Lecture**

KN-12 3D-printed affinity and biomimetic sorptive phases: A new area of bioselective sorbents

Manuel Miró, María Pau García-Moll, and Enrique Javier Carrasco-Correa

9:20 **Oral Communications**

9:20 **O-14 Microwave-assisted sample preparation in food analysis: A highly valuable ally**

MILESTONE
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Giorgia Purcaro

9:35 **O-15 Determination of time-weighted average concentrations of volatile organic pollutants in the air based on solid-phase microextraction by a modified sampler with an alternative geometry**

Nassiba Baimatova, Olga P. Ibragimova, Anara Omarova, Kazbek Tursun, and Bauyrzhan Bukenov

9:50 **O-16 Comprehensive investigation of different coatings and adsorbents for SPME and their influence on analytical performance**

Frank Michel, Deyny D. Mendivelso, Olga I. Shimelis, and Robert E. Shirey

10:05 **O-17 On-site quantification of transformation products of unsymmetrical dimethylhydrazine in environmental samples using solid-phase microextraction and gas chromatography**

Bulat Kenessov, Bauyrzhan Bukenov, Anel Kapar, Tolkyn Kurmanbayeva, and Nargiz Kazhkenova

10:20 **Keynote Lecture**

KN-13 Microextraction techniques: A powerful tool for (bio)markers extraction in non-invasive diagnostic methodologies. Colorectal cancer as a real case

Lorena Vidal, Iván Rubio, David Guill-Berbegal, Antonio Canals, and Rodrigo Jover

10:40 **Keynote Lecture**

KN-14 Matrix solid-phase dispersion: From laboratory applications to pilot scale operation

Elena Stashenko

11:00 **Coffee Break. Sponsors Exhibition. Poster Session 2 (Espejos Room)**

Auditorium

Plenary Session
Chairs: Alberto Chisvert[1] and Barbara Bojko[2]
[1]University of Valencia (Spain), [2]Nicolaus Copernicus University in Torun (Poland)

12:00 **Plenary Lecture**

PL-02 Advances in the design and production of sorbent materials for sample preparation

Jared L. Anderson

Auditorium

Young Oral Session 5
Chairs: José Manuel Herrero-Martínez[1] and Adrián Gutiérrez-Serpa[2]
[1]University of Valencia (Spain), [2]Dresden University of Technology (Germany)

12:40 **Young Oral Communications**

12:40 **YO-16 Pore-networked membranes for the microextraction of personal care products and pharmaceuticals in environmental water**

Idaira Pacheco-Fernández, Zaoming Wang, Yamil J. Colón, and Shuhei Furukawa

12:55 **YO-17 Recycling of cellulose acetate from cigarette filters and its application in water treatment**

Massimo Giuseppe De Cesaris, Lorenzo Antonelli, Giovanni D'Orazio, Iolanda Francolini, and Alessandra Gentili

13:10 **YO-18 Lab in a bottle: An affordable and portable approach for environmental analysis**

Francisco Antonio Casado-Carmona, Rafael Lucena, and Soledad Cárdenas

Atenas Room

Young Oral Session 6
Chairs: Henryk H. Jeleń[1] and Rafael Lucena[2]
[1]Poznań University of Life Sciences (Poland), [2]University of Córdoba (Spain)

12:40 **Young Oral Communications**

12:40 **YO-19 New developments in coated blade spray-mass spectrometry for high-throughput and rapid analysis**

Wei Zhou and Janusz Pawliszyn

12:55 **YO-20 Development of SPE-CE methods for the determination of active pharmaceuticals ingredients in an industrial manufacturer's wastewater**

Emma O'Sullivan-Carroll, Anna Hogan, Stewart Howlett, Carmel Pyne, Paul Downing, Angela Moriarty, Marguerite Lynch, and Eric Moore

13:10 **YO-21 Biosensing platform based on the combination of zeolite imidazolate framework and luciferase for rapid point-of-care of urinary tract infection**

Héctor Martínez-Pérez-Cejuela, Maria Maddalena Calabretta, Ernesto Francisco Simó-Alfonso, José Manuel Herrero-Martínez, and Elisa Michelini

13:30 **Symposium Lunch (Cleopatra Restaurant)**

15:00 **Sponsors Exhibition. Poster Session 2 (Espejos Room)**

Auditorium

Oral Session 5: Advanced Microextraction Strategies
Chairs: Abdul Malik[1] and Lorena Vidal[2]
[1]University of South Florida (USA), [2]University of Alicante (Spain)

15:45 **Keynote Lecture**

KN-15 Recent advances and future trends in molecularly imprinted polymers-based sample preparation

Myriam Díaz-Álvarez, Esther Turiel, and Antonio Martín-Esteban

16:05 **Oral Communications**

16:05 **O-18 Paper-supported solvents as sustainable extractant phase**

Guillermo Lasarte-Aragonés, Inmaculada López-Ruiz, Ceren H. Bozmaoglu, Mehmet Gumustas, Rafael Lucena, and Soledad Cárdenas

16:20 **O-19 A flower-shaped polymeric-coated cellulose paper for the isolation of organic contaminants from aqueous matrices**

Khwanchanok Samkampang, María Laura Soriano-Dotor, Chongdee Thammakhet-Buranachai, Rafael Lucena, and Soledad Cárdenas

16:35 **O-20 The use of polymer inclusion membranes (PIMs) as sorbents for the preconcentration of antibiotics from natural waters**

Berta Alcalde, Enriqueta Anticó, and Clàudia Fontàs

Atenas Room

Oral Session 6: Green Analytical Chemistry
Chairs: Soledad Cárdenas[1] and Torsten C. Schmidt[2]
[1]University of Córdoba (Spain), [2]University of Duisburg-Essen (Germany)

15:45 **Keynote Lecture**

KN-16 Micromotors in action as environmental micro-cleaners: Just a concept or a futuristic reality?

Alberto Escarpa and Beatriz Jurado

16:05 **Oral Communications**

16:05 **O-21 AGREE and AGREEprep – Tools for greenness assessment in analytical chemistry**

Marek Tobiszewski

16:20 **O-22 Methods of analyzing biological material assessed using the WAC and ChlorTox Scale metric tools**

Renata Wietecha-Posłuszny and Paweł Mateusz Nowak

16:35 **O-23 33 years of SPME – A review from manufacturer's perspective**

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Frank Michel

Auditorium

Young Oral Session 7
Chairs: Priscilla Rocío-Bautista[1] and Giulia Mastellone[2]
[1]University of Jaén (Spain), [2]University of Turin (Italy)

17:10 **Young Oral Communications**

17:10 **YO-22 Extraction of persistent organic pollutants from environmental water samples using a dynamic covalent polymer**

Javier González-Sálamo, Cecilia Ortega-Zamora, David Santana, Romen Carrillo, and Javier Hernández-Borges

17:25 **YO-23 Exploring the potentialities of a starch-based biodegradable polymer in white analytical chemistry: Study on the extraction of emerging contaminants from water samples**

Barbara Benedetti, Henry MacKeown, Matteo Baglietto, Chiara Scapuzzi, Marina Di Carro, and Emanuele Magi

17:40 **YO-24 Recycled polylactic acid-based nanocomposites for water remediation and sample pretreatment**

Lorenzo Antonelli, Elena Lucci, Riccardo De Santo, Maria Chiara Frondaroli, Chiara Dal Bosco, and Alessandra Gentili

17:55 **YO-25 Biorefinery approach for the revalorization of leaves from *Citrus reticulata* to obtain antioxidant and anticholinergic extracts**

Gloria Domínguez-Rodríguez, Víctor Manuel Amador-Luna, Beatriz Rodríguez-Luzardo, Pablo Mendoza-Orbaneja, Fabián Parada-Alfonso, and Elena Ibáñez

Atenas Room

Young Oral Session 8

Chairs: Marek Tobiszewski[1] and Alberto Escarpa[2]

[1]Gdańsk University of Technology (Poland), [2]University of Alcalá (Spain)

17:10 **Young Oral Communications**

17:10 **YO-26 Sample preparation metric of sustainability. A new tool to assess analytical sample preparation procedures**

Adrián Gutiérrez-Serpa, Raúl González-Martín, Verónica Pino, and Muhammad Sajid

17:25 **YO-27 How to analyse fatty acids and fatty acid methyl esters in water samples simultaneously**

Lucie K. Tintrop, Jana R. Lieske-Overgrand, Kaliyani Wickneswaran, Rukiyye Abis, Ruth Brunstermann, Maik A. Jochmann, and Torsten C. Schmidt

17:40 **YO-28 Miniaturized stir bar sorptive dispersive microextraction as a high-throughput and feasible approach for low-availability samples**

Cristian Azorín, Juan L. Benedé, and Alberto Chisvert

17:55 **YO-29 High-throughput and automated solid-phase microextraction-liquid chromatography-mass spectrometry system for the analysis of mycotoxins in beers**

Martyna N. Wieczorek, Wei Zhou, and Janusz Pawliszyn

20:15 **Gala Dinner (Cleopatra Swimming Pool Terrace)**

Friday, 21st July 2023

Auditorium

Oral Session 7: Food Analysis

Chairs: Cecilia Cagliero[1] and Alessandra Gentili[2]

[1]University of Turin (Italy), [2]Sapienza University of Rome (Italy)

9:00 **Keynote Lecture**

KN-17 Sustainable analytical strategies for multiresidue/multiclass monitoring of emerging risks in complex samples

Ana M. García-Campaña, María del Mar Aparicio-Muriana, María del Mar Delgado-Povedano, Laura Carbonell-Rozas, Rocío Carmona-Molero, Maykel Hernández-Mesa, Monsalud del Olmo-Iruela, Laura Gámiz-Gracia, and Francisco J. Lara

9:20 **Oral Communications**

9:20 **O-24 Sample preparation and GC×GC a powerful marriage in food analysis**

Giorgia Purcaro, Grégory Bauwens, Steven Mascrez, and Damien Eggermont

9:35 **O-25 Development of green strategies for the extraction-encapsulation of antioxidant carotenoids from persimmon peels**

Merichel Plaza and María Luisa Marina

9:50 **O-26 Simultaneous and sequential combination of orthogonal techniques for the sustainable and comprehensive extraction of proteins and polyphenols from malt rootlets**

María Concepción-García, Ester Hernández-Corroto, and María Luisa Marina

10:05 **O-27 Untargeted analysis of dairy products using vacuum-assisted techniques coupled with gas chromatography – mass spectrometry (GC–MS)**

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MARKES international

Rachael Szafnauer, Rebecca Cole, Lucy Hearn, and Anna Kling

10:20 **O-28 A simple method for pesticide residues determination in green vegetables based on QuEChERS extraction technique coupled with GC-MS/MS and LC-MS/MS**

Klaudia Pszczolińska, Dominika Lalek, Barbara Kociołek, and Agnieszka Krzyżanowska

10:40 **Keynote Lecture**

KN-18 Challenges in extraction of aroma compounds from food matrices

Henryk H. Jeleń, Martyna Wieczorek, and Małgorzata Majcher

Atenas Room

Oral Session 8: Bioanalysis

Chairs: Jared L. Anderson[1] and María J. Trujillo-Rodríguez[2]

[1]Iowa State University (USA), [2]University of La Laguna (Spain)

9:00 **Keynote Lecture**

KN-19 Solid-phase microextraction and thin-film microextraction for direct and indirect characterization of organs' quality – A new avenue in transplant surgery

Natalia Warmuzińska, Kamil Łuczykowski, Iga Stryjak, Dagmar Kollmann, Peter Urbanellis, Markus Selzner, and Barbara Bojko

9:20 **Oral Communications**

9:20 **O-29 Study of derivatization conditions for determination of SCFAs by HS-SPME-GC/MS: Strengths and limitations**

Érica A. Souza-Silva, María Bajo-Fernández, Laura Mayo, M. Fernanda Rey-Stolle, Vanessa Alonso-Herranz, Antônia Garcia, and Coral Barbas

9:35 **O-30 Electromembrane microextraction (EME) of parabens and their main hydroxy metabolites in maternal urine and amniotic fluid**

Noemí Aranda-Merino, Eduardo Leo-Martos, Miguel Ángel Bello-López, Rut Fernández-Torres, and María Ramos-Payán

9:50 **O-31 Use of untargeted metabolomic to identify salivary biomarkers of Sjögren's syndrome**

Pauline Bosman, Valérie Pichon, Ana Carolina Acevedo, Hélène Chardin, and Audrey Combès

10:05 **O-32 Determination of microplastics related pollutants in human organs**

Rosa Peñalver, María Dolores Pérez-Álvarez, Natalia Arroyo-Manzanares, Natalia Campillo, and Pilar Viñas

10:20 **O-33 An improved miniaturized device to enhance the enrichment factors in liquid-phase microextraction: Application to the simultaneous extraction of polar and non-polar acids in biological samples**

Alejandro Martín, Noemí Aranda-Merino, Rut Fernández-Torres, Miguel Ángel Bello-López, and María Ramos-Payán

10:40 **Keynote Lecture**

KN-20 Sustainable sample pretreatment for microplastic analysis in environmental samples

Torsten C. Schmidt, Mike Wenzel, Gerrit Renner, and Jochen Tuerk

11:00 **Coffee Break. Sponsors Exhibition (Espejos Room)**

Auditorium

Closing Plenary Session
Chairs: Janusz Pawliszyn[1] and Elena Stashenko[2]
[1]University of Waterloo (Canada), [2]Industrial University of Santander (Colombia)

12:00 **Closing Plenary Lecture**

PL-03 The role of (bio)polymeric phases in extending the sustainability of sample preparation

Soledad Cárdenas

12:40 **Presentation of ExTech2024 – Closing Ceremony and Awards**

13:30 **Symposium Cold Lunch (Espejos Room)**

15:00 **Trip to El Teide National Park**

Wednesday, 19th July 2023

POSTER SESSION 1

11:00 - 12:00 h and 15:00 - 15:45 h
All presenters should be at their poster during the poster session
PS1 posters should be removed on Wednesday evening after 18:00 h
Any poster remaining after 18:30 h will be discarded

TOPIC 1: ENVIRONMENTAL ANALYSIS

P-01 **Enhanced extraction protocols for recent emerging organic contaminants adsorbed onto microplastics**

Ludovit Schreiber, Zoraida Sosa-Ferrera, Sarah Montesdeoca-Esponda, Sergio Santana-Viera, Nicolas Milan Michalides, Laura Santi, and José Juan Santana-Rodríguez

P-02 **Microwave-assisted extraction of antidepressants from fish tissue**

Sergio Santana-Viera, Águeda Alameda-Cuesta, Sarah Montesdeoca-Esponda, Ludovit Schreiber, Zoraida Sosa-Ferrera, and José Juan Santana-Rodríguez

P-03 PFAS screening and quantitation with SPME and direct ionization with DART mass spectrometry

Pedro Cano, Miguel Ángel Pérez, William Fatigante, Brian D. Musselmann, Elena Bueno, Ronald V. Emmons, Aghogho A. Olomukoro, and Emanuela Gionfriddo

P-04 Determination of tetracyclines in wastewater using an automated method for the solid-phase extraction followed by fluorimetric detection

María Alejandra Vargas-Muñoz, Edwin Palacio, Gemma Turnes-Palomino, Jean-Luc Boudenne, Bruno Coulomb, and Fabien Robert-Peillard

P-05 Determination of microplastics in Cuvierian tubules and digestive tracts of the sea cucumber *Holothuria sanctori* from Tenerife (Canary Islands, Spain)

Gloria Navalón-Alajarín, Cristina Villanova-Solano, Cintia Hernández-Sánchez, and Javier Hernández-Borges

P-06 Optimization of an analytical method based on micro-matrix solid-phase dispersion combined with gas chromatography-mass spectrometry for the determination of nine bisphenols in mussel samples

Nieves Carro, Rebeca Fernández, Isabel García, María Ignacio, and Ana Mouteira

P-07 Optimization of micro-QuEChERS extraction coupled to gas chromatography-mass spectrometry for a fast determination of phthalates in mussel samples

Nieves Carro, Rebeca Fernández, Sergio Sóñora, Julio Cobas, Isabel García, María Ignacio, and Ana Mouteira

P-08 Sample preparation analysis methods of microplastics

Raffaella Mossotti, Giulia Dalla Fontana, and Tiziano Battistini

P-09 Pipette tip solid-phase microextraction packed with graphene nanoplatelets and smartphone-based fluorescence detection to determination of sulfonamides in environmental waters

Diego Barzallo, Edwin Palacio, and Laura Ferrer

P-10 3D-printed device coated with Zn/Co-ZIF for the on-site extraction of fluoroquinolones from water samples prior to HPLC-FL analysis

Diego Barzallo, Neus Crespí, Andrea Están, Carlos Palomino, Gemma Turnes, Edwin Palacio, and Laura Ferrer

P-11 POPs extraction from marine microplastics - Factors that reduce extraction efficiency

Bárbara Abaroa-Pérez, Daura Vega-Moreno, and J. Joaquín Hernández-Brito

P-12 Microplastics identification in chocolate using micro-spectroscopy techniques

Elena Battaglini, Michelina Soccio, Maurizio Fiorini, and Nadia Lotti

P-13 Automated, highly sensitive analysis of target residual fumigants in coffee by multi-step enrichment–headspace–trap (MSE–HS–trap) coupled with GC–MS for regulatory food safety testing

Rachael Szafnauer and Lucy Hearn

P-14 Determination of steroid hormones adsorb on microplastics from the Macaronesia

Javier Pacheco-Juárez, Sarah Montesdeoca-Esponda, Rayco Guedes-Alonso, María Esther Torres-Padrón, Zoraida Sosa-Ferrera, and José Juan Santana-Rodríguez

P-15 Assessment of the presence of synthetic hormones in stranded cetaceans

Adrián Bullón-Téllez, Javier Pacheco-Juárez, Zoraida Sosa-Ferrera, José Juan Santana-Rodríguez, Natalia García-Álvarez, Jesús De la Fuente, Manuel Arbelo, Antonio Fernández, and Rayco Guedes-Alonso

P-16 Determination of bisphenols, parabens, benzophenone-3 and triclosan in human urine by liquid chromatography coupled with tandem mass spectrometry

Borja Peris-Camarasa, Pablo Dualde, and Clara Coscollà

P-17 PEsticide Reduction using Friendly and Environmentally Controlled Technologies: PERFECT LIFE project results

Esther Fuentes, Héctor Calvete-Sogo, Amalia Muñoz, Patricia Chueca, Cruz Garcerá, Fabrizio Gioelli, Marco Grella, Paolo Marucco, Emilio Gil, Jordi Llop, José Castro, Antonio López, Egon Cervera, Sébastien Codis, Xavier Delpuech, Guillermo Vidal, and Clara Coscollà

P-18 Relevant hyphenated techniques to study volatile organic compounds for the development of biobased materials from seaweeds

Jérôme Bauta, Léa Rivière, Guadalupe Vaca-Medina, Antoine Rouilly, Virginie Vandenbossche, Christine Raynaud, and Valérie Simon

P-19 Chemical speciation of cadmium in water samples by magnetic carbon nanotubes-based solid-phase microextraction

Sol Cotaimich-Díaz, José A. López-López, and Carlos Moreno

P-20 Multidetermination of benzophenone and derivatives in sunscreen by direct-immersion solid-phase microextraction and gas chromatography–mass spectrometry

Andrés J. Rascón, Priscilla Rocío-Bautista, Laura Palacios-Colón, Juan Francisco García-Reyes, and Evaristo Ballesteros

P-21 Assessment of chlorinated pesticide content in eggs and milk consumed in rural Roma communities in Transylvania, Romania, and their risk to human health

Vlad Alexandru Pănescu, Mihail Simion Beldean-Galea, Mihaela Cătălina Herghelegiu, Victor Bocoș-Binținţan, Maria-Virginia Coman, and Vidar Berg

P-22 Towards a high efficiency electromembrane system for cadmium analysis in water at sub-ppb levels

Carolina Mendiguchía, Macarena Silva, and Carlos Moreno

P-23 Extraction and analysis of phenolic compounds in *Phaeodactylum tricornutum* cells in Cu polluted cultures

Paula Santiago-Díaz, Milagros Rico, Argimiro Rivero, Melchor González-Dávila, and Magdalena Santana-Casiano

P-24 Determination of residues of pharmaceutical active compounds in water samples – Optimization of the analytical method

Dariusz Drożdżyński, Adam Perczak, Marek Szczepański, Klaudia Pszczolińska, and Rafał Motała

P-25 An analytical method to quantify volatile methylsiloxanes from microplastics

Tiago Ferreira, Vera Homem, and Nuno Ratola

P-26 Extraction and derivatization of arsenic trichloride and arsenous acid in water and soil samples for gas chromatography coupled with mass spectrometry analysis

Mariana Mikic, Charlotte Desoubries, Cécile Montauban, Marie Spiandore, Marie Gaïao-Lousa, Christine Albaret, and Emmanuel Joubert

P-27 Evaluation of the occurrence of pesticides and their transformation products associated with olive groves in surface waters using UHPLC-Orbitrap-MS suspect screening

Alfonso Fernández-García, Ana B. Martínez-Piernas, David Moreno-González, Bienvenida Gilbert-López, and Juan F. García-Reyes

P-28 Optimizing the solvent extraction of soil lipid components related to the organic matter hydrophobic character

Gladys Arteaga-Clemente, Marta Selma Garzón-Molina, María Araceli García-González, and Mónica González-González

P-29 Polymer inclusion membranes (PIMs) for the screening of metal pollution in natural waters

Berta Alcalde, Enriqueta Anticó, and Clàudia Fontàs

P-30 **Effective removal of N-nitrosodiphenylamine from aqueous media using dead leaves of seagrass as a low-cost adsorbent**

Mazen K. Nazal, Durga Rao Gijjapu, and Nabeel Abuzaid

P-31 **Application of TD/Py-GCxGC-TOFMS for analysis of microplastics & chemical pollutants in ambient particulate matter samples**

Stephanie Wright, Joseph Levermore, Nick Jones, and Julio Lluch

TOPIC 2: NEW EXTRACTION TECHNOLOGIES

P-32 **A sampling platform incorporating 3D-printed paddles-stirrers coated with metal-organic framework MIL-100(Fe) for *in-situ* extraction of phenolic pollutants in biodigester supernatant and wastewater effluent samples**

María Alejandra Vargas-Muñoz, Carlos Palomino, Gemma Turnes-Palomino, and Edwin Palacio

P-33 **Extraction of proteins with dendronized magnetic nanoparticles**

David Rincón-Montón, Ester Hernández-Corroto, Rafael Gómez, Francisco Javier de la Mata, Javier Sánchez-Nieves, Jesús Cano, María Luisa Marina, and María Concepción García

P-34 **Dyes and solvents in pen inks: Analytical methods for solving court cases**

Daura Vega-Moreno, Óscar Díaz-Santana, Nuria Cárdenes-Sánchez, Patricia Ordóñez-Merencio, and Miguel Á. Suárez de Tangil Navarro

P-35 **Improvement of the saponification process for mineral oil analysis using microwave-assisted saponification/extraction**

Gregory Bauwens, Donatella Ferrara, and Giorgia Purcaro

P-36 **Synergistic combination of green technologies for antioxidant phenolic compound extraction from orange by-products**

Roberto Tejedor-Ajenjo, Merichel Plaza, and María Luisa Marina

P-37 **A new approach to sample preparation in electroanalytical methods: Nitro compounds adsorbed in a MWCNT bucky paper electrodic platform**

José Carbajo, Raúl Moscoso, A. Poblete, and Juan A. Squella

P-38 **Aptamer-functionalized 3D-cylinder-shaped printed devices for in-vial microextraction of β-lactoglobulin prior to capillary electrophoresis-mass spectrometry**

Laura Pont, María Vergara-Barberán, José Manuel Herrero-Martínez, Fernando Benavente, and Enrique Javier Carrasco-Correa

P-39 **Analysis of α-synuclein by on-line aptamer affinity solid-phase extraction direct mass spectrometry**

Laura Pont, Hiba Salim, Estela Giménez, and Fernando Benavente

P-40 **Determination of total petroleum hydrocarbons in water by solid-phase extraction (SPE) using shungite as sorbent: Green and efficient approach**

Bauyrzhan Abdykarimov, Aibat Ibraimov, and Mereke B. Alimzhanova

P-41 **Polymeric films modified with deep eutectic solvents for organophosphorus pesticides extraction from water samples**

Ivonne Quintanilla, Clàudia Fontàs, and Enriqueta Anticó

P-42 **Unleashing the potential of 3D-printing containing rare-earth metal-organic frameworks as fluorescence sensors for the determination of tetracyclines in seawater**

Laura Alcázar-Escobedo, Noelia Campillo-Tamarit, Ernesto Francisco Simó-Alfonso, and Enrique Javier Carrasco-Correa

P-43 **Bisphenol A extraction using tailored 3D-printed stir-sticks modified with a selective aptamer**

Alba Roselló-Carrió, Patricia Reboredo-Rodríguez, María Jesús Lerma-García, José Manuel Herrero-Martínez, and Enrique Javier Carrasco-Correa

P-44 **Use of paper-based devices modified with polyhedral oligomeric silsesquioxane-methacryl substituted monolith for the extraction of bisphenols from environmental samples**

María López-Escoín, Miriam Beneito-Cambra, José Manuel Herrero-Martínez, and María Jesús Lerma-García

Young Posters

TOPIC 1: ENVIRONMENTAL ANALYSIS

YP-01 ***In-vitro* bioaccesability of hazardous chemicals coming from rubber recycled tire using simulated biological fluids**

Sergio Sóñora, Andrés Duque-Villaverde, Daniel Armada, Thierry Dagnac, and María Llompart

YP-02 **Particles from tire rubber: Determination of hazardous chemical agents**

Andrés Duque-Villaverde, Daniel Armada, Thierry Dagnac, and María Llompart

YP-03 **Determination of hazardous compounds from tire rubber in water using solid-phase microextraction (SPME)**

Andrés Duque-Villaverde, Lúa Vázquez, Daniel Armada, Thierry Dagnac, and María Llompart

YP-04 Extraction of emerging organic pollutants from polyethylene and polypropylene microplastics

Gabriel Jiménez-Skrzypek, Rachele Lusiardi, Cecilia Ortega-Zamora, Javier González-Sálamo, and Javier Hernández-Borges

YP-05 Untargeted screening and risk assessment of semi-volatile organic compounds in Spanish household dust: Pilot study

Esther Fuentes, Pablo Miralles, Antonio López, María Ibáñez, and Clara Coscollà

YP-06 Vacuum headspace solid-phase microextraction analysis of pesticides in grapes

Yerkanat A. Syrgabek and Mereke B. Alimzhanova

YP-07 Optimization of an extraction procedure to assess contaminants of emerging concern in freshwater invasive species

Diana Manjarrés-López, Dyana Vitale, Sandra Callejas-Martos, Yolanda Picó, Nicola Montemurro, and Sandra Pérez

YP-08 Multisorbent extraction and HRMS DIA based quantification method for the analysis of wastewater-borne pollutants in temporary rivers

Olga Gómez-Navarro, Francesc Labad, Diana Manjarrés-López, Nicola Montemurro, and Sandra Pérez

YP-09 Extraction of emerging organic pollutants from seawater and wastewater from Tenerife (Canary Islands, Spain) using an automated solid-phase extraction system

Gabriel Jiménez-Skrzypek, Julia Méndez-Catalán, Javier González-Sálamo, and Javier Hernández-Borges

YP-10 Determination of 11 antibiotics in fish samples by QuEChERS-UHPLC-MS/MS

Yousra Aissaoui, Gabriel Jiménez-Skrzypek, Javier González-Sálamo, Malika Trabelsi-Ayadi, Javier Hernández-Borges, and Ibtissem Ghorbel-Abid

YP-11 Exposure and risk assessment to airborne dl-PCBs, dioxins and furans in the population living in the neighborhood of a cement plant: A pilot study in the Valencian Region (Spain)

Iñaki Lacomba, Pablo Ruiz, Antonio López, Cristina Socas-Hernández, and Clara Coscollà

YP-12 PFASs in paper- and cardboard-based food contact materials

Pablo Miralles, María Isabel Beser, Yovana Sanchís, Cristina Socas-Hernández, and Clara Coscollà

YP-13 Identification of unknown substances in the ambient air of medical care centers surroundings in the Valencian Region (Spain)

Esther Fuentes, Antonio López, María José Mora, Jordi Blasco, Gema Barber, and Clara Coscollà

YP-14 Optimization of a solid-phase extraction procedure to determine a wide range of per- and polyfluoroalkyl substances (PFAS) by LC-HRMS in drinking waters from the Basque Country

Maddi Ibañez, Anne San Román, Amaia Irizar, Eunate Abilleira, Juan F. Ayala-Cabrera, Belén González-Gaya, and Nestor Etxebarria

YP-15 Target and suspect screening analysis of water-accommodated fractions of crude oil using HS-SPME-GC-MS

Carles Moreu-Romero, Anabella Massa, Juan F. Ayala-Cabrera, Esther Blanco-Rayón, Mireia Irazola, Urtzi Izagirre, Leire Mijangos, Pamela Ruiz, and Ionan Marigómez

YP-16 Determination of lambda-cyhalothrin in air and its metabolites in urine after conventional and innovative applications in citrus and vineyard crops

Esther Fuentes, Patricia Chueca, Cruz Garcerá, Marco Grella, Fabrizio Gioelli, Paolo Maruco, Amalia Muñoz, Héctor Calvete-Sogo, Antonio López, Esther Borrás, Teresa Vera, María Ibáñez, and Clara Coscollà

YP-17 Microplastics determination in soils of Teide National Park (Tenerife, Canary Islands, Spain)

Cristopher Domínguez-Hernández, Santiago Gómez-Escabia, Sergio J. Álvarez-Méndez, Francisco Javier Díaz-Peña, and Javier Hernández-Borges

YP-18 Integrating coated blades into environmental samplers: On-site extraction and direct mass spectrometric determination of emerging organic pollutants

Francisco Antonio Casado-Carmona, Rafael Lucena, and Soledad Cárdenas

YP-19 Determination of microplastics in a membrane bioreactor-based wastewater treatment plant

Adrián Manuel Afonso-Álvarez, Luisa María Vera-Peña, and Javier Hernández-Borges

YP-20 *Cymodocea nodosa* seagrass meadow as microplastics sink: Description and quantification

Cristina Villanova-Solano, Silvia Oliva, José Carlos Mendoza-Durán, Cintia Hernández-Sánchez, Carmen B. de los Santos, and Javier Hernández-Borges

YP-21 **Determination of microplastics in three species of sea urchins (*Paracentrotus lividus*, *Arbacia lixula* and *Diadema africanum*) from different coastal localities of Tenerife and La Palma (Canary Islands, Spain)**

Cristina Villanova-Solano, Marta Sevillano-González, Valentina León-Pérez, Cintia Hernández-Sánchez, Francisco Javier Díaz-Peña, Javier González-Sálamo, and Javier Hernández-Borges

YP-22 **Ultrasound-assisted extraction followed by liquid chromatography and tandem mass spectrometry for the simultaneous determination of 9 herbicides in soil**

Ana Castiñeira-Landeira, Lúa Vázquez, Helena González-Leirado, María Llompart, and Thierry Dagnac

YP-23 **Quantification of volatile methylsiloxanes in water samples using liquid-liquid extraction assisted by sonication and GC-MS**

Diego W. Allgaier-Díaz, Tiago Ferreira, Vera Homem, Verónica Pino, Juan H. Ayala, and Nuno Ratola

TOPIC 2: NEW EXTRACTION TECHNOLOGIES

YP-24 **Assessing the potentialities of an easy-to-use sample treatment strategy: Multivariate investigation on "Moka extraction" of typical ingredients from dietary supplements**

Matteo Baglietto, Barbara Benedetti, Marina Di Carro, and Emanuele Magi

YP-25 **DUT-52 metal-organic framework as sorbent for contaminants of emerging concern in micro-dispersive solid-phase extraction: Pros and cons**

Eduardo Lodoso-Ruiz, María J. Trujillo-Rodríguez, Jorge Pasán, Juan H. Ayala, and Verónica Pino

YP-26 **Green and effective procedures of biological samples preparation for the determination of psychoactive substances**

Paweł Stelmaszczyk, Daniel Rojas, Alberto Escarpa, and Renata Wietecha-Posłuszny

YP-27 **An emerging extraction technique based on micro-solid-phase extraction followed by GC-MS analysis for quantification of opium alkaloids in poppy seed infusion**

Gema Casado-Hidalgo, Rosa Perestelo, Sonia Morante-Zarcero, José S. Câmara, and Isabel Sierra

YP-28 **Multiplex extraction of four emerging contaminant families through 3D-printed stir-towers incorporating metal-organic frameworks**

Francisco Mestre-Manrique, Miriam Beneito-Cambra, and Enrique Javier Carrasco-Correa

YP-29 Perovskites: New extraction materials with luminescent properties for preconcentration and sensing of emerging pollutants

Francisco Mestre-Manrique, Rocío Expósito-Hernández, Carolina Fernández-Saiz, Miriam Beneito-Cambra, and Enrique Javier Carrasco-Correa

YP-30 A dual liquid/solid-phase microextraction system using carbon nanotubes for cadmium extraction from water samples

Senia Cuervo-Novas, Carolina Mendiguchía-Martínez, and Carlos Moreno

YP-31 Determination of lysozyme in foods using aptamer-based hybrid affinity monolith in paper-based devices

Natalia Piqueras-García, María Vergara-Barberán, María Jesús Lerma-García, Ernesto Francisco Simó-Alfonso, and José Manuel Herrero-Martínez

YP-32 Aptamer-modified elastic 3D-printed springs for enhanced extraction of lactoferrin in food samples

Natalia Piqueras-García, Yvonne de Ligt, José Manuel Herrero-Martínez, María Jesús Lerma-García, and Enrique Javier Carrasco-Correa

YP-33 Sustainable 3D-printed devices modified with aluminium-based metal-organic frameworks for extraction of picolinic herbicides from environmental waters

Alejandro Gil-Aparicio, Enrique Javier Carrasco-Correa, and José Manuel Herrero-Martínez

YP-34 Enhanced extraction of sulfonamides from environmental waters using sustainable 3D-printed devices coated with ZIF-8

Alejandro Gil-Aparicio, Enrique Javier Carrasco-Correa, and José Manuel Herrero-Martínez

YP-35 Extraction and characterization of microRNA from food wastes and seaweeds: Evaluation of anti-inflammatory properties

Miriam Guzmán-Lorite, Rafael Liñán-Atero, Laura Muñoz-Moreno, María José Carmena, María Luisa Marina, and María Concepción García

YP-36 Beware of vector-borne diseases widespreading. An automated molecular diagnostic workflow to detect and differentiate them

Enrique Lucia-Lobera, Brisa H. Santos, Laura Pastor, Carlota Giménez, and María Concepción Gil

YP-37 New molecular diagnosis workflow for antimicrobial resistance detection and timing improvement in sepsis management

Enrique Lucia-Lobera, Maialen Alza, Brisa H. Santos, Laura Pastor, and Carlota Giménez

YP-38 Revalorization of garlic (*Allium sativum* L.) by-products by pressurized liquid extraction

Ignacio Jiménez-Amezcua, Jana Merino, Andrea Martín-Ortiz, Marina Díez-Municio, Ana Cristina Soria, María L. Sanz, and Ana I. Ruiz-Matute

YP-39 Hypercrosslinked β-cyclodextrins polymer as sustainable sorbent for the extraction of persistent organic pollutants from environmental water

Nina Felli, Alessandra Gentili, Luisa Maria Migneco, Iolanda Francolini, and Javier Hernández-Borges

YP-40 Vertical introducing bio-compatible solid-phase microextraction pin to mass spectrometry using probe electrospray ionization interface for high sensitivity and low matrix effect analysis

Wei Zhou and Janusz Pawliszyn

YP-41 Mixed-mode cationic exchange sorptive tapes combined with mass spectrometry for determining drugs of abuse in saliva samples

Carlos Calero-Cañuelo, Francisco Antonio Casado-Carmona, Rafael Lucena, and Soledad Cárdenas

Thursday, 20th July 2023

POSTER SESSION 2

11:00 - 12:00 h and 15:00 - 15:45 h
All presenters should be at their poster during the poster session
PS2 posters should be removed on Thursday evening after 18:00 h
Any poster remaining after 18:30 h will be discarded

TOPIC 3: BIOANALYSIS, *IN-VIVO* ANALYSIS, METABOLOMICS AND NATURAL PRODUCTS

P-45 Simultaneous determination of thymine, uracil and 5-fluorouracil in human plasma samples by hollow fiber liquid-phase microextraction at-line coupled with capillary electrophoresis

Noemí Aranda-Merino and Pavel Kubáň

P-46 Development of two-steps extraction technique and LC-QTOF method for determination of cortisol and its metabolites in human plasma and animal faeces

Anna Stachniuk, Alicja Trzpil, Rafał Łopucki, Daniel Klich, Wanda Olech, and Emilia Fornal

P-47 An ecological, economical and efficient method for drug determination in blood samples

Alicja Chromiec, Klaudia Ordon, and Renata Wietecha-Posłuszny

P-48 **Application of solid-phase extraction (SPE) with HPLC-DAD for analysis of the concentration of oxidative stress markers in urine of women with overweight after a 4-week energy-restricted ketogenic diet**

Natalia Bączek, Joanna Topolska, and Natalia Drabińska

P-49 **Optimization of ionization process of steroid metabolites with the use of Design of Experiments approach**

Julia Jacyna, Magdalena Buszewska-Forajta, Joanna Raczak-Gutknecht, Michał J. Markuszewski, and Danuta Siluk

P-50 **Mass spectrometry-based multiplatform method for untargeted metabolomic analysis of gastrointestinal stromal tumour**

Szymon Macioszek, Danuta Dudzik, Agnieszka Wozniak, Patrick Schoffski, and Michal J. Markuszewski

P-51 **Electromembrane microextraction (EME) of dialkyl phosphate metabolites in biological samples**

Juan Manuel Ávila-García, Noemí Aranda-Merino, Isabel Moreno, Miguel Ángel Bello-López, Rut Fernández-Torres, and María Ramos-Payán

P-52 **SPME analysis of *Lacticaseibacillus paracasei* M_{12} and its prospects in the fight against *Erwinia amylovora***

Mereke B. Alimzhanova, Elvira Ismailova, Akmeir Elubaeva, Aibat Ibraimov, and Amankeldy Sadanov

P-53 **The forensic toxicology use of ion-pair reversed-phase HPLC with UV detection in two fatal cases of sodium nitrite poisoning**

Joanna Dawidowska, Małgorzata Wacławik, Bartosz Wielgomas, Michał J. Markuszewski, and Michał Kaliszan

TOPIC 4: FOOD ANALYSIS

P-54 **Development of an aptasensor to determine Concanavalin A in food samples**

Lara Vives-Julve, Miriam Beneito-Cambra, María Vergara-Barberán, José Manuel Herrero-Martínez, María Jesús Lerma-García, and Ernesto Francisco Simó-Alfonso

P-55 **Characterization of leaves, stem and roots of *Artemisia thuscula* for potential food and pharmaceutical applications**

Paula Santiago-Díaz, Ihintza Arakistan-Urtzelai, Milagros Rico, and Argimiro Rivero

P-56 **Headspace sampling technique to enhance the volatile chromatographic fingerprint of foods**

Steven Mascrez, Damien Eggermont, and Giorgia Purcaro

P-57 Application of solid-phase microextraction for the analysis of aroma compounds generated during ripening of tomatoes fruits treated with synthetic immunity inducers

Małgorzata Majcher, Patryk Frąckowiak, and Aleksandra Obrępalska-Stęplowska

P-58 In-solution trypsin digestion and LC-QTOF method for the identification of peptide markers differentiating meat species in processed food products

Anna Stachniuk, Alicja Trzpil, Klaudia Szałaj, Anna Kozub, Magdalena Montowska, and Emilia Fornal

P-59 Nicarbazin determination in glassy carbon electrode modified with multiwall carbon nanotube bucky paper

Juan A. Squella, Carlos Lema, Alejandro Álvarez, and Raúl Moscoso

P-60 Determination of bisphenols and related compounds in honey and bee pollen samples

Silvia Valverde, Beatriz Martín-Gómez, Lucía Alcaide, José Bernal, and Ana María Ares

P-61 Two-step continuous SPE system with enhanced matrix removal sorbent combined with UHPLC-MS/MS for the determination of parabens and phenolic compounds in dairy products

Laura Palacios-Colón, Andrés J. Rascón, Beatriz Puebla-Domínguez, and Evaristo Ballesteros

P-62 Simultaneous determination of steroids and NSAIDs in milk and eggs collected from rural Roma communities in Transylvania, Romania based on DLLME-SFO and HPLC analysis

Mihail Simion Beldean-Galea, Mihaela Cătălina Herghelegiu, Vlad Alexandru Pănescu, Victor Bocoș-Binținţan, Maria-Virginia Coman, and Vidar Berg

P-63 A multi-step sample preparation coupled with gas chromatography-mass spectrometry for the quantification of rotundone in grapes

Thomas Baerenzung dit Baron, Laura Lescot, Daria Asieieva, Alban Jacques, Olivier Geffroy, and Valérie Simon

P-64 A direct comparison of applying helium & hydrogen carrier gases with HS-SPME-GC-TOF-MS analysis of aroma active compounds in whisky

Nick Jones, Julio Lluch, Colton Myers, Jason Hetrick, Simona Nicoara, and Geraint Morgan

P-65 Aroma profiling of coffee varieties and blends to investigate quality and authenticity via automated high-capacity sorptive extraction (HiSorb) with GC–MS

Josh Marshall, Massimo Santoro, Rachael Szafnauer, Lucy Hearn, Rebecca Cole, Jan Peter Mayser, Laura McGregor, and Ericka Hachmeister

TOPIC 5: GREEN ANALYTICAL CHEMISTRY

P-66 Hydrophobic natural deep eutectic solvents based on L-menthol as supported liquid membrane for hollow fiber liquid-phase microextraction of triazines from environmental water samples

Myriam Díaz-Álvarez and Antonio Martín-Esteban

P-67 Synthesis and evaluation natural deep eutectic solvents (NADES) in the development of a sustainable extraction method of triazines in agricultural soils

Myriam Díaz-Álvarez, Antonio Martín-Esteban, and Esther Turiel

P-68 Preliminary evaluation of natural deep eutectic solvents for the ultrasound-assisted extraction of sulfonamides from soil samples

Ana Isabel García-Valcárcel and Antonio Martín-Esteban

P-69 A liquid microextraction based one-step method for the chemical fractionation of copper in seawater

Ibtissem Belbachir, José A. López-López, Belén Herce-Sesa, and Carlos Moreno

P-70 Multivariate aluminium metal-organic frameworks as adsorption materials in analytical microextraction

Alicia H. Hinojal, María J. Trujillo-Rodríguez, Juan H. Ayala, Verónica Pino, and Jorge Pasán

P-71 Automated determination of iodate using the iodine-starch reaction: A Lab-In-Syringe method

Cemre Yildiz, Sercan Yildirim, Petr Solich, and Burkhard Horstkotte

TOPIC 6: NEW EXTRACTION PHASES

P-72 Comparison of two novel ionic liquids modified-monoliths in spin columns for the extraction of β-blockers from urine

María Celia García-Álvarez-Coque, Óscar Mompó-Roselló, Ernesto Francisco Simó-Alfonso, María José Ruiz-Ángel, and José Manuel Herrero-Martínez

P-73 Development of galactose-functionalized methacrylate polymeric materials for selective extraction of food allergen lectins

María Vergara-Barberán, María Jesús Lerma-García, Ernesto Francisco Simó-Alfonso, and José Manuel Herrero-Martínez

P-74 Development of an aptamer-based stir bar sorptive extraction for the determination of β-lactoglobulin in food using MALDI-TOF-MS

María Vergara-Barberán, Natalia Piqueras-García, Ernesto Francisco Simó-Alfonso, Fernando Benavente, María Jesús Lerma-García, and José Manuel Herrero-Martínez

P-75 **Introducing an environmentally friendly method for detecting aflatoxins in pistachios: An innovative approach utilizing deep eutectic solvents**

Andrea Schincaglia, Alberto Cavazzini, Giorgia Purcaro, and Marco Beccaria

P-76 **Determination of polyaromatic hydrocarbons in wastewater using triazole functionalized silica sorbent based stir bar-supported micro-solid-phase extraction coupled with gas chromatography-mass spectrometry**

Khalid Alhooshani and Abdulkadir Tanimu

P-77 **Enhanced cup-shaped 3D-printed devices with dual stirring positions for solid-phase extraction of fluoroquinolones**

Miriam Beneito-Cambra and Enrique Javier Carrasco-Correa

P-78 **A chromia-based sorbent for the enrichment of phosphotyrosine biomarker**

Mohamed Rashad, Abdullah Alhendal, Laila Alshatti, Ali Husain, and Ali Bumajdad

P-79 **Exploiting natural materials as sorptive phases in rotating-disk sorptive extraction**

Pablo Richter, Daniel Arismendi, Alejandra Molina, Inés Ahumada, and Iván Vera

P-80 **Simultaneous determination of thyroid hormones in serum using BioSPME for sample preparation**

Frank Michel and Olga I. Shimelis

P-81 **Metal-organic framework-modified paper-based for extraction of neonicotinoids in water samples**

José Manuel Herrero-Martínez, Mónica Catalá-Icardo, Lluis Illana-Sánchez, Carmen Gómez-Benito, Sagrario Torres-Cartas, Susana Meseguer-Lloret, and Ernesto Francisco Simó-Alfonso

Young Posters

TOPIC 3: BIOANALYSIS, *IN-VIVO* ANALYSIS, METABOLOMICS AND NATURAL PRODUCTS

YP-42 **Metal-organic frameworks as sorbents for the antidepressant vortioxetine via miniaturized dispersive solid-phase extraction and high-performance liquid chromatography with diode array detection**

Miguel Á. Martínez-Briones, Isaac Negrín-Santamaría, María. J. Trujillo-Rodríguez, Juan H. Ayala, Jorge Pasán, and Verónica Pino

YP-43 **Determination of the modification of *Lactuca sativa* L. leaves' metabolic profile due to the presence of bisphenol A in the hydroponic media by UAE-GC-MS**

Jerónimo Cabrera-Peralta and Araceli Peña-Álvarez

YP-44 Levels of 16 urinary phthalate metabolites in adult population of Valencia Region (Spain)

Pablo Dualde, Borja Peris-Camarasa, Pablo Miralles, and Clara Coscollà

YP-45 Analytical assessment of forage quality: A case study on native flora from Fuerteventura (Canary Islands, Spain)

Raquel Pérez-Reverón, Adolfo Perdomo-González, Javier Hernández-Borges, Covadonga Rodríguez-González, José Antonio Pérez-Pérez, and Francisco Javier Díaz-Peña

YP-46 Employing the statistical experimental design for the optimization of low volume-SPME for analysis of volatile organic compounds in exhaled breath condensate by GC-MS

Natalia Drabińska and Martyna Natalia Wieczorek

YP-47 Automated microfluidic open interface for direct coupling of solid-phase microextraction to mass spectrometry to facilitate rapid and high-throughput analysis

Wei Zhou, Emir Nazdrajić, and Janusz Pawliszyn

YP-48 Comparison of different stationary phases of solid-phase extraction (SPE) for efficient isolation of 8-isoprostane and 8-hydroxyguanosine from exhaled breath condensate and urine

Joanna Topolska, Natalia Bączek, and Natalia Drabińska

YP-49 Harnessing the potential of natural compounds through DES-based DLLME to make greener fragrance analysis: A case study with high water content samples

Gaia Bechis, Giulia Mastellone, Arianna Marengo, Barbara Sgorbini, Patrizia Rubiolo, and Cecilia Cagliero

YP-50 Metal-organic frameworks and biopolymers for the extraction of anthraquinones and chromones in aloe vera gel via miniaturized dispersive solid-phase extraction and high-performance liquid chromatography with diode array detection

Sara Lara-Torres, María J. Trujillo-Rodríguez, Jorge Pasán, Juan H. Ayala, and Verónica Pino

YP-51 Solid-phase immunoextraction followed by liquid chromatography-tandem mass spectrometry for the selective determination of thyroxine in human serum

Víctor Vállez-Gomis, Juan L. Benedé, Audrey Combès, Alberto Chisvert, and Valérie Pichon

YP-52 High-throughput determination of oxidative stress biomarkers in saliva by solvent-assisted dispersive solid-phase extraction for clinical analysis

Guillem Peris-Pastor, Sandra Alonso-Rodríguez, Juan L. Benedé, and Alberto Chisvert

YP-53 Octanol-supported wooden tips: Porous sorptive phases and organic solvent holders in microextraction

Jaime Millán-Santiago, Saloua Hammadi, Latifa Latrous El Atarche, Rafael Lucena, and Soledad Cárdenas

YP-54 Natural materials and hypodermic needles in ambient ionization mass spectrometry: Affordable and disposable ESI emitters in bioanalysis

Jaime Millán-Santiago, Rafael Lucena, and Soledad Cárdenas

YP-55 Encapsulation efficiency determination methods for the analysis of autoantigenic peptides within phosphatidylserine-liposomes

Irene Latorre, Montserrat Mancera-Arteu, Oumaima El Ouahabi, Míriam Salvadó, Bruna Barneda-Zahonero, Sílvia Rodríguez-Vidal, and Victoria Sanz-Nebot

YP-56 Isolation of PS-liposomes from biological samples by size exclusion chromatography and subsequent characterization

Oumaima El Ouahabi, Montserrat Mancera-Arteu, Irene Latorre, Míriam Salvadó, Bruna Barneda-Zahonero, Sílvia Rodríguez-Vidal, and Victoria Sanz-Nebot

YP-57 Characteristics of mixed chitosan-bioglass coatings on plasma activated PEEK polymer

Kacper Przykaza, Małgorzata Jurak, Grzegorz Kalisz, Robert Mroczka, and Agnieszka Ewa Wiącek

YP-58 A non-invasive colorectal cancer diagnostic method based on a solid-phase microextraction technique for the determination of organic compounds from fecal samples

Iván Rubio, David Guill, Rodrigo Jover, Antonio Canals, and Lorena Vidal

YP-59 LC/MS determinations of kynurenine pathway metabolites in saliva

Alicja Trzpil, Anna Stachniuk, Klaudia Szałaj, Anna Kozub, and Emilia Fornal

YP-60 Characterization of the aromatic profile of *Passiflora Edulis* Sims from Canary Islands (Spain) using solid-phase microextraction: A tool to discriminate new vegetive materials

Montse Saura-Cayuela, María J. Trujillo-Rodríguez, Juan H. Ayala, José M. García-Fraga, María J. Grajal-Martín, Arminda C. Peña-Dorta, and Verónica Pino

TOPIC 4: FOOD ANALYSIS

YP-61 LC-QTOF discovery of metabolomic markers for the quality control of sunflower and rapessed oils

Alicja Trzpil, Agata Sumara, Anna Stachniuk, Klaudia Szałaj, Anna Kozub, and Emilia Fornal

YP-62 Shotgun mass spectrometry for qualitative and quantitative assessment of lipidomic profiles of several edible oils

Kacper Przykaza, Hanna Nikolaichuk, Anna Kozub, Jolanta Tomaszewska-Gras, and Emilia Fornal

YP-63 Extraction and determination of curcumins and gingerols in ginger and turmeric nutraceuticals with validated UHPLC-DAD method

Michaela Sanderová, Eliška Hujová, and Dalibor Šatínský

YP-64 On-line SPE-HPLC determination of ochratoxin a in ice and straw wine and phenolic compounds profiling

Pavlína Moravcová and Dalibor Šatínský

YP-65 Development and application of an organo-silica membrane functionalised with amino groups for the determination of macrolide antibiotics in eggs

Lorena González-Gómez, Sonia Morante-Zarcero, Damián Pérez-Quintanilla, Gema Paniagua-González, Rosa M. Garcinuño, Pilar Fernández-Hernando, and Isabel Sierra

YP-66 Monofloral honey analysis using vacuum-assisted HS-SPME

Madina Mamedova, Mereke B. Alimzhanova, and Yerkanat A. Syrgabek

YP-67 Optimization of a solid-phase microextraction gas chromatography-mass spectrometry method for volatile profiling of aromatized extra virgin olive oils

Irene Custureri, Sergio Rivas, Angelo Maria Giuffrè, Vincenzo Sicari, and Ana Cristina Soria

YP-68 Application of liquid-liquid extraction for LC/MS-based authentication of camelina seed oil

Anna Kozub, Anna Stachniuz, Alicja Trzpil, Hanna Nikolaichuk, Kacper Przykaza, Jolanta Tomaszewska-Gras, and Emilia Fornal

YP-69 LC-MS profiling of gluten extracts from model bread dough supplemented with phenolic acids

Anna Kozub, Piotr Sosnowski, Klaudia Szałaj, Agnieszka Nawrocka, and Emilia Fornal

YP-70 Ultrasound-assisted extraction, purification by solid-phase extraction with sulfonic acid-functionalized SBA-15 and HPLC-MS/MS analysis for the quantification of opium alkaloids in ground poppy seeds

Gema Casado-Hidalgo, Sonia Morante-Zarcero, Damián Pérez-Quintanilla, and Isabel Sierra

TOPIC 5: GREEN ANALYTICAL CHEMISTRY

YP-71 Evaluation of new ferrofluidic materials for the extraction of chiral pesticides from environmental water, followed by enantioselective liquid chromatography analysis coupled with tandem mass spectrometry

Elena Lucci, Lorenzo Antonelli, Chiara Dal Bosco, Salvatore Fanali, Bezhan Chankvetadze, and Alessandra Gentili

YP-72 Copper and nickel preconcentration by a dispersive liquid-liquid microextraction method using a hydrophobic deep eutectic solvent

Beatriz Gómez-Nieto, Elena Serna-Martín, María Jesús Gismera, María Teresa Sevilla, and Jesús R. Procopio

YP-73 Efficiency of natural deep eutectic solvents to extract phenolic compounds from tea samples by a micro-ultrasonic-assisted extraction

Laura Carbonell-Rozas, Roberto Romero-González, and Antonia Garrido-Frenich

YP-74 Optimization of natural deep eutectic solvent-microwave-assisted extraction of birch (*Betula* sp.) bark bioactives

Inmaculada Luque-Jurado, María L. Sanz, and Ana Cristina Soria

YP-75 Comparison of microwave-assisted extraction and subcritical water extraction to obtain anti-aging extracts from a brewer's waste

Rafael Liñán-Atero, Miriam Guzmán-Lorite, María Luisa Marina, and María Concepción García

YP-76 Optimization of green extraction techniques for determination of bisphenols in human breast milk samples via HPLC-FLD

Szymon Szubartowski and Tomasz Tuzimski

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YP-82 Enhanced extraction of bisphenol analogues in environmental waters using automated systems in combination with 3D-printed millifluidic devices containing metal-organic frameworks and molecularly imprinted polymers

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YP-83 3D-printed devices and molecularly imprinted polymers for riboflavin extraction and detection in food samples: A smartphone-based colorimetric sensor

Roser Payà-Pou, Beatriz Fresco-Cala, Miriam Beneito-Cambra, Ernesto Francisco Simó-Alfonso, and Enrique Javier Carrasco-Correa

YP-84 Evaluation of natural deep eutectic solvents for the selective extraction and stability enhancement of bioactive compounds from saffron (*Crocus sativus*)

Adal Mena-García, Juan Matute-Pinos, María L. Sanz, Marina Díez-Municio, and Ana I. Ruiz-Matute

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Alejandro Rodríguez-González, María J. Trujillo-Rodríguez, Ana I. Jiménez-Abizanda, Nabeel M. Abbas, Jared L. Anderson, and Verónica Pino

YP-86 *In-situ* growth of metal-organic frameworks onto braid silver fibers as novel devices for solid-phase microextraction

Isaac Negrín-Santamaría, Adrián Gutiérrez-Serpa, María J. Trujillo-Rodríguez, Jorge Pasán, and Verónica Pino

YP-87 Green extraction of phenolic compounds from olive leaves: Investigating deep eutectic solvents

Aina Mir-Cerdà, Mercè Granados, Sonia Sentellas, and Javier Saurina

YP-88 Polyphenols recovery from natural deep eutectic solvent extracts using polymeric resins: Searching strategies for sustainable extraction

Aina Mir-Cerdà, Dipa Dey, Javier Saurina, Sonia Sentellas, José Luis Beltrán, and Mercè Granados

YP-89 Metal-organic frameworks as solid-phase sorbents in different formats for the isolation of synthetic cannabinoids in oral fluids

Héctor Martínez-Pérez-Cejuela, Patricia García-Atienza, Ernesto Francisco Simó-Alfonso, José Manuel Herrero-Martínez, and Sergio Armenta-Estrela

YP-90 Pillared-layer CIM metal-organic frameworks: Improved strategies for analytical microextraction

Patricia I. Napolitano-Tabares, Yaiza Martín-García, Ana B. Lago, Ana I. Jiménez-Abizanda, Jorge Pasán, and Verónica Pino

YP-91 Mixed-matrix membranes based on a metal-organic framework and recycled polystyrene and their use in thin-film microextraction for the determination of personal care products

Irina Guerra-Martín, Adrián Gutiérrez-Serpa, Ana I. Jiménez-Abizanda, Jorge Pasán, and Verónica Pino

YP-92 Metal-organic frameworks in matrix solid-phase dispersion for the extraction of phytochemicals from *Cannabis sativa* L. samples

Giacomo Giaccardi, Giulia Mastellone, María J. Trujillo-Rodríguez, Jorge Pasán, Cecilia Cagliero, and Verónica Pino

YP-93 PVC-diphenilamine covalent bonding supported on cellulose for opioids extraction from saliva samples

Ana M. Pedraza-Soto, Carlos Calero-Cañuelo, Rafael Lucena, and Soledad Cárdenas

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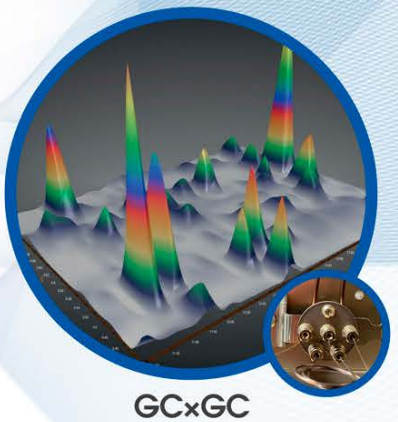

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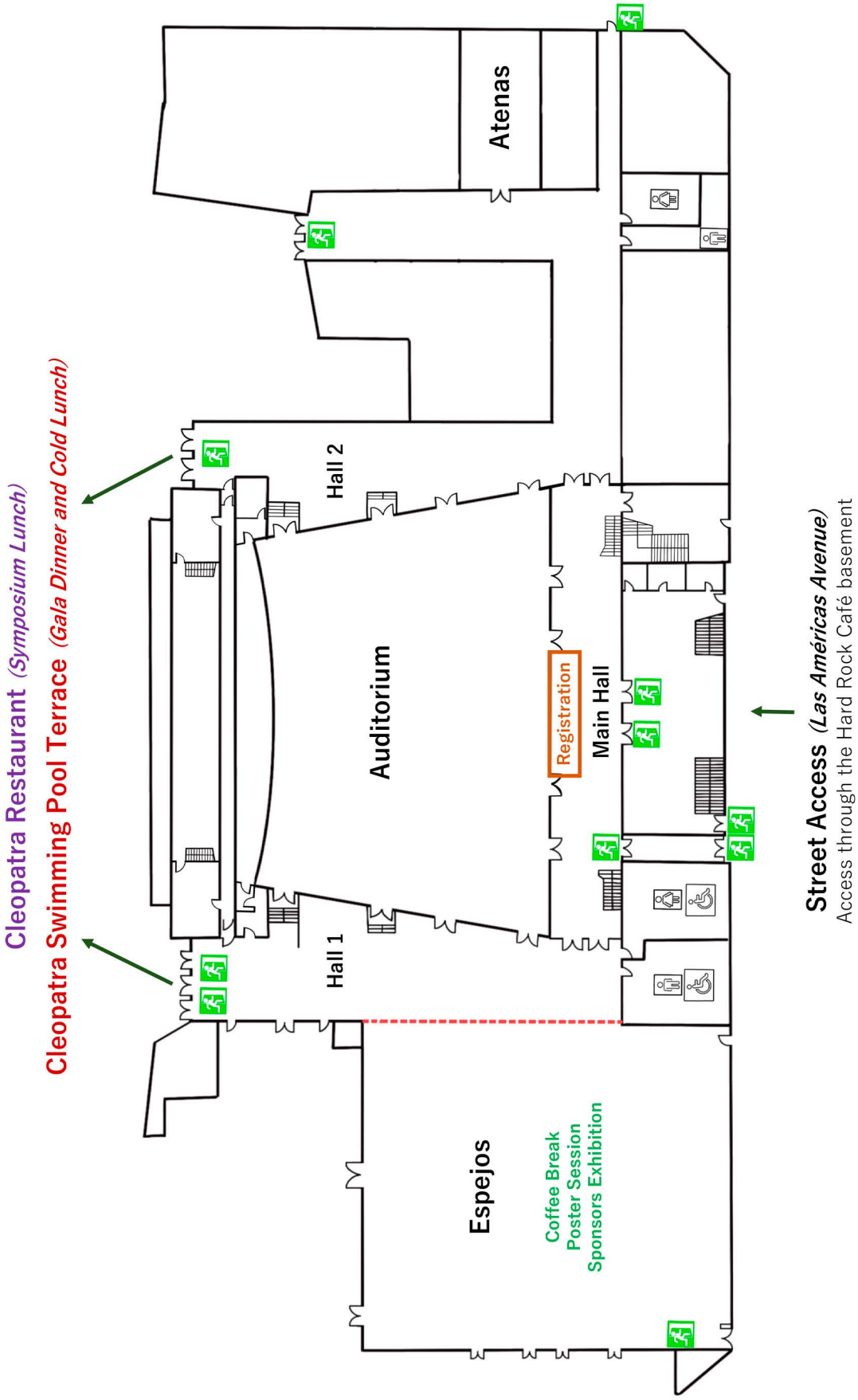

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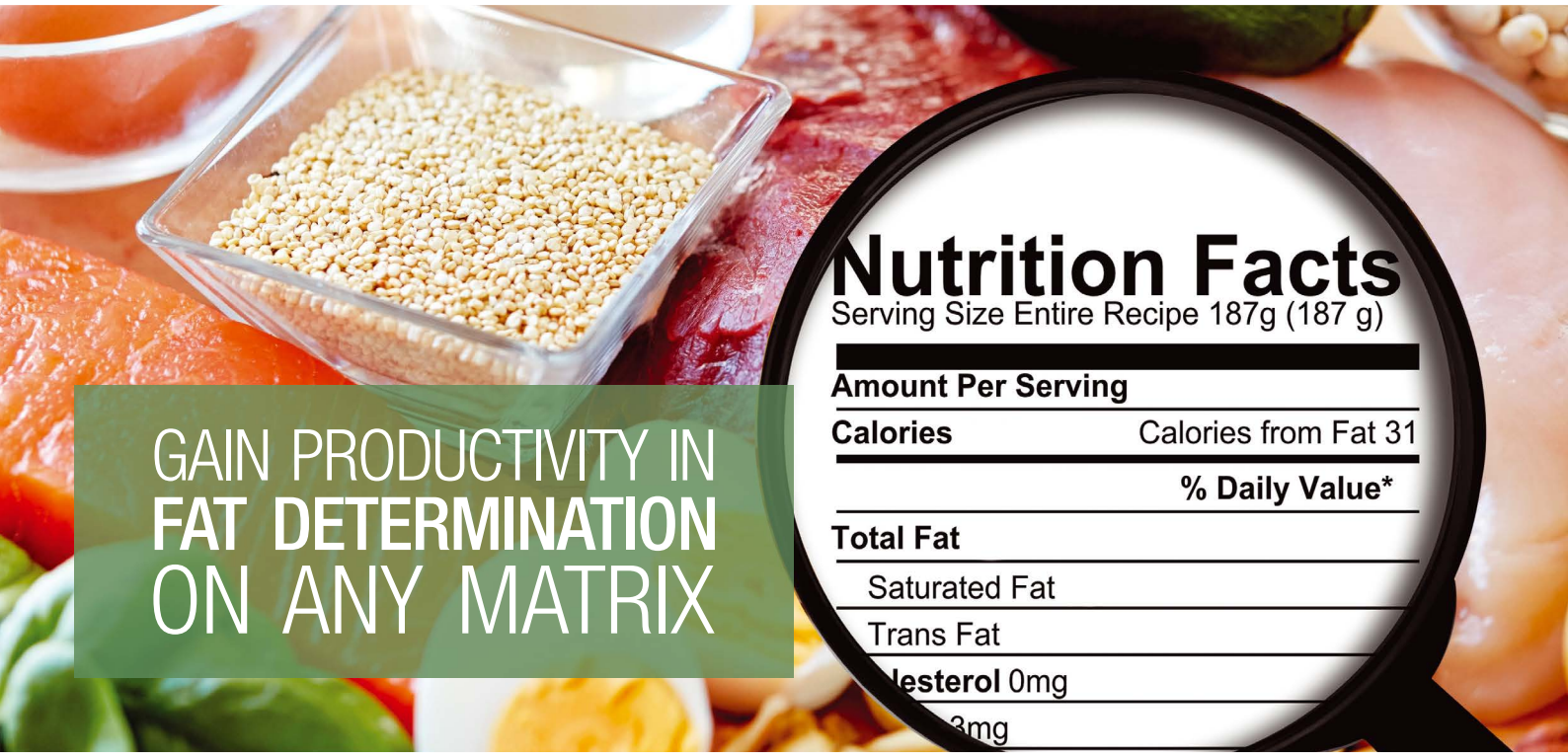

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PLENARY LECTURES

PL-01

Think big but design small and efficient, a green path of microextractions

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Keywords: *Microextractions, Fundamentals, Solid-phase microextraction, Liquid-phase microextraction*

Non-exhaustive microextraction came into the field of analytical chemistry with the introduction of solid-phase microextraction (SPME) in 1990 [Anal. Chem. 62 (1990) 2145-2148]. Exhaustive extraction performed in small scale also defined as microextraction has been discussed even earlier. Microextraction is therefore not a new concept as this term has been used in our field for over 30 years. Microextractions encompasses a group of extraction techniques using miniaturized format and in case of non-exhaustive version it refers to the system in which the extraction phase (liquid or solid) is substantially smaller than the sample volume, and where the amount of extraction phase, typically <100 µL or<10 mg and therefore does not facilitate transfer of majority of analytes to the extraction phase [Pure Appl. Chem. 88 (2016) 517–558]. While SPME has been at the forefront of non-exhaustive microextraction research since its introduction, other microextraction techniques have been developed in parallel, such as liquid phase microextraction (LPME) including electromembrane extraction (EME) [J. Chromatogr. A 1109 (2006) 183-190]. In fact, microextraction has been a very active area of research; a search in Scopus identifies approximately 27,000 articles with “microextraction” in the title, abstract, or in the keywords. Undoubtedly, the prolific research carried out in this area over the past 30 years has substantiated the unique properties of microextraction; a) related to performance (high pre-concentration and selectivity, soft extraction); b) compatibility (direct injection into GC and LC); c) flexibility (in field, in-vivo, automation, microchip); and d) sustainability (solvent-free, low consumption of reagents and materials).

Although the field of microextraction has been developed over three decades, the potential is much greater. As understanding about microextraction fundamentals and advantages evolves, the next generations of analytical scientists will realize the full potential of current microextraction research. Inside analytical laboratories, young scientists concerned about sustainability, have opportunity to take advantage of the greenness afforded by microextraction techniques. In addition, innovative researchers have opportunity to apply new analytical chemistry tools for challenging applications in biology, where they can explore the ‘soft’ microextraction feature of the technique to minimize disturbances to biochemical equilibria and living systems in in-vivo experiments. Outside analytical laboratories, young scientists have opportunity to explore miniaturized analytical instruments as well as drones, microfluidics, smartphones and other hand-held devices. These technologies will enable on-site measurements by persons not trained in analytical chemistry. However, the portable detectors in most of the cases cannot measure target analytes directly in blood, food, wastewater, etc. and therefore some efficient sample preparation is required. Research results indicates that preferred sample preparation in many applications would involve microextraction, as the preferred alternative.

In this presentation, the focus will be on the historical scientific development of non-exhaustive microextractions as in SPME and LPME. We will also discuss our efforts to facilitate commercialization and adoption of the techniques by regulatory agencies. The presentation will provide guidance and perspective on trends for young scientists interested to explore the microextraction in their research careers.

Acknowledgements
We are grateful to the Natural Sciences and Engineering Research Council (NSERC) of Canada for their financial support to develop SPME technology.

PL-02

Advances in the design and production of sorbent materials for sample preparation

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Keywords: *Magnetic ionic liquids, Polymeric ionic liquids, Nucleic acids, Sample preparation, 3D printing*

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 within sample preparation. 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. We will also demonstrate the use of MILs for the extraction of nucleic acids from plants, where very minimal sample pretreatment of the plant sample is required. Finally, recent work in using three-dimensional (3D) printing technologies for the batch production of sorbent materials for solid-phase microextraction and thin-film microextraction will be presented. Using a simple modification to a commercial desktop printer, 3D printed devices comprised of PILs can be printed to have very high repeatability among devices printed within the same batch as well as different batches.

PL-03

The role of (bio)polymeric phases in extending the sustainability of sample preparation

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Keywords: *(Bio)polymeric phases, Natural resources, Sustainable sample preparation*

The inclusion of sustainability criteria is a priority in any human activity and is perfectly identified in the Sustainable Development Goals (SDGs). The 17 SDGs describe sustainability as a broad concept that encompasses not only environmental aspects, but also social (quality of life) and economic (economic growth). A detailed evaluation of the 169 targets derived from them highlights the importance of pollution control in environmental compartments, food quality or health care, which are all linked to obtaining information to support decision-making.
Researchers working in the field of analytical chemistry are aware of the important role they play in this context, as well as the need for their actions to be aligned with the sustainability concept, which goes beyond the term "green", which is limited to the environmental aspects of the measurement processes. The greatest impact of sample analysis directly related to the preparation step. On the one hand, it is the largest source of reagent consumption, energy and waste generation. On the other hand, it has a major impact on the quality of the result, as it is the main source of error.
Understanding the importance of sustainability in its broadest sense, sample preparation has incorporated these priorities in its evolution that has been progressively focused on the incorporation of natural sorbents for analytes isolation to develop greener approaches. The role that biopolymers may play in preparing novel and effective sorbent materials in sample preparation has been clearly pointed out in recent years. These (bio)polymeric phases, taken in its widest meaning include substances of different nature that can be used as sorbent/substrates, e.g. polysaccharides, proteins, or DNA.
(Ligno)cellulosic materials (viz. paper, cotton, wood or cork) are especially attractive in this context since both, the resulting sorptive phase and the synthetic pathway remain simple, sustainable and affordable. These materials can be used either raw or functionalized to promote specific interactions with the analytes. Considering their different shapes (planar, fibrous, or tips) they are also complementary in terms of microextraction format and instrumental coupling.
These aspects are the main topic of this communication with the aim of providing a general view of their potential in microextraction techniques, their compatibility with both spectroscopic and spectrometric techniques and their contribution to the sustainability of sample preparation.

Acknowledgements
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KEYNOTE LECTURES

KN-01

Smart materials and low-cost supports: A well-matched couple for sample preparation

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Keywords: *Hybrid materials, Metal-organic frameworks, Aptamers, Cheap formats, 3D printing*

Smart materials in analytical chemistry can be defined as those tailored, task-specific, or designed materials, sometimes mimicking the nature, that provide significant enhancement of practical properties. Over the past decade, the scientific community has focused on developing novel functional materials with smart and advanced characteristics, greatly contributing to the enhancement of conventional analytical methods, especially regarding sample treatment, in terms of selectivity, sensitivity and analytical method miniaturization. In this sense, smart solid materials have been used in (bio)analysis sample preparation including materials based on antibody-antigen interactions, molecularly imprinted polymers, aptamers, carbon-based nanomaterials, metal-organic frameworks, and hybrid materials, among others. On the other hand, there is a widespread interest in developing simple, cheap and sustainable analytical methodologies that promote the development and application of these types of materials. In this work, novel (micro)extraction devices based on the combination of these smart materials with conventional extraction formats (such as cartridges, micropipette tips, microcentrifuge tubes, etc) as well as in small common lab supports (tubing, magnetic stir bars, among others) are presented. Apart from these supports, there is a need to continue developing easier-to-use devices with enhanced performance addressed to face the current analytical challenges. In this context, emerging formats such as 3D-printed objects and paper-based devices have emerged onto the scene in recent years. The combination of these formats with smart materials will also be addressed. For this purpose, representative analytical applications that use some of these materials in the different low-cost designed devices will be described. Additionally, the future prospects offered by this fruitful pairing in the field of sample treatment will be outlined.

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KN-02

New miniaturized approaches for the analysis of low-availability samples

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Keywords: *Sample preparation, Microextraction, Low-availability samples, Biomarkers, Biological fluids*

Sample amount may be a challenge when the analysis of biological matrices is performed. Giving aside urine and blood, large volumes of biological fluids are often not available either because of the nature of the sample itself (e.g., saliva, semen, follicular fluid, or cerebrospinal fluid) or because of the characteristics of the person under study (e.g., newborns, immunosuppressed or anemic patients). This drawback gets worse if the target compounds are at trace level. Furthermore, biological matrices usually comprise many compounds with very diverse nature that make them really complex samples to deal with. As a consequence, these matrices require more or less time-consuming sample pretreatments, but on the contrary, bioanalysis requires rapid and affordable methods that enable the analysis of a vast number of samples in clinical laboratories every day. So, besides of classical inputs related less consume of solvents/reagents and less generation of wastes, additional inputs are being demanded related with the development of sample treatment procedures that minimize the amount of sample needed for the analysis and, at the same time, that allow high-throughput analysis and are easily portable.
This talk presents in a summarized way different approaches recently developed by our research group to overcome these challenges when trace compounds need to be determined in low-availability samples. These approaches derive mainly from dispersive sorbent-based microextraction techniques, in such a way the sorbent material is dispersed into the sample, and later retrieved by using different strategies having a common denominator, i.e., the use of magnetic sorbents and magnets to handle them. These approaches have been used to determine different biomarkers in different scenarios as a proof-of-concept, such as testosterone in saliva from athletes, cortisol in serum from preterm newborns, and cortisol and cortisone in saliva, providing excellent features from both the analytical and clinical points of view.

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KN-03

Synthesis of novel hybrid nanocomposites based on clay coated by physical vapor deposition for solid-phase microextraction of emergent pollutants from aqueous samples

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Keywords: *Solid-phase microextraction, R.F. magnetron sputtering, Lab-made fibers, β-ciclodextrine, Emergent pollutants*

Solid-phase microextraction (SPME), introduced in 1990 by Arthur and Pawliszyn, is a technique that integrates sampling, isolation, and concentration of analytes into one step. SPME is widely used as sample preparation for chromatographic techniques for metabolomics, pharmaceutics, agriculture, food, or water analysis. The SPME system involves a coated fiber inside a septum-piercing needle, where the coating is the key component of the technique. The coating in commercial devices is an absorbent or a mix of them firmly bonded to the substrate and must be chemically and thermally stable. Commonly used coatings include polydimethylsiloxane (PDMS), polyethylene glycol (PEG, carbowax), and polyacrylate. Despite its wide use, there are several issues that involve the coatings that hinder the microextraction processes, like lack of specificity, poor mechanical properties, low re-use, high carry-over, phase bleed, and high commercialization cost. This work aims to overcome some of the drawbacks mentioned above with the design, production, and synthesis of lab-made fibers. The methodology involves: 1) deposition of MMT (k-10 Aldrich) clay over nitinol fibers by magnetron sputtering, 2) on-fiber peroxidation with H_2SO_4/H_2O_2 to form aluminol and silanol groups, and 3) on fiber esterification with citric acid and β-cyclodextrin (βCD) (methodology proposed by Sánchez et al.), also we synthetized the Linford fibers for a reference point. Our interest in using the magnetron sputtering technique lies in the thin (nanometric) layers, the homogeneity, and the mechanical resistance of the coating. On the other hand, βCD is a cyclic polymer recognized for its ability to form chemical equilibria (inclusion complexes) that increase the adsorption of the material by non-covalent bonding interactions, which can be undone at high temperatures to release the trapped molecules. In the preliminary results, it has been observed by gas chromatography with FID detector (GC-FID) that the fibers do not present signals *per se*, although a prior thermal cleaning must be carried out to eliminate the volatiles from the silicone used for assembly. So, they are suitable for microextraction processes. This way, we obtain the green light to continue with the analysis of the extraction capacity of these fibers compared to commercial fibers for a wide range of analytes. It has been reported the first extrusion system for lab-made fibers and its assembling.

Acknowledgements
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KN-04

Sustainable miniaturized sample preparation strategies to assess the global impact of recycled tire crumb rubber microplastics

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Keywords: *Recycled crumb rubber, Microplastics, Football fields, Hazardous chemicals, Sample preparation, Chromatography-mass spectrometry*

Social and environmental concern about the use of crumb rubber from end-of-life car tires in the construction of different sport and recreational facilities is increasing due to the release of hazardous chemicals. This topic is included as one of the "hot topics" of the ECHA "Granules and mulches on sports pitches and playgrounds" [https://echa.europa.eu/hot-topics/granules-mulches-on-pitches-playgrounds]. The microplastic material constitutes the first intended source of microplastics into the environment. Actually, the rubber granules (granular infill) used on sports pitches is the largest single source of pollution with estimated releases of up to 16,000 tonnes per year.
In this project, different analytical strategies dealing with this pollution problem will be presented, including the crumb rubber itself, and the environmental compartments (water, air). Occurrence of classical persistent organic pollutants such as PAHs or phthalates is assessed, as well as that of other "new emerging pollutants" such as 6PPD-quinone, which has demonstrated high toxicity to some aquatic species. The proposed methods are based on ultrasound extraction, solid-phase extraction and microextraction, and on the combination of some of these techniques followed by GC-MS/MS and LC-MS/MS analysis. The complexity of this material and the continuous entry of hazardous compounds into the environment will be proven. In addition, in-vitro bioaccesibility assay will demonstrate for the first time the human oral bioaccesibility of some of these hazardous chemicals.

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KN-05

On-site environmental extraction devices based on open-source technologies

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Keywords: *On-site extraction, Environmental waters, Portability, Simplicity*

On-site extraction is a useful approach in environmental water analysis as it simplifies the overall analytical method and increases the sample throughput. In contrast to the standard analytical workflow, based on sampling and sample transportation to the laboratory, on-site extraction simplifies the logistics and improves the sample representativeness by stabilizing the analytes during transportation and storage. Due to their reduced size, microextraction techniques are especially relevant for on-site extraction. This communication overviews one decade of research in our group dedicated to novel devices in this context. The speed of the extraction, the portability of the apparatus, and the affordability of the sorptive phases (SPs) have been the driving forces in the evolution of this research line.

Stirring-based devices, where the SPs are stirred into the samples, have been preferred over other alternatives since they can promote the isolation of the target compounds from the samples. The stirring efficiency has been demonstrated as a critical factor for extraction performance, considering that relatively high sample volumes (in the liter range) are processed for better representativeness. Initially, commercial drills were used as stirring elements since they can provide high stirring rates. However, due to their quite expensive price and their high energy consumption, they have been ultimately substituted by miniaturized motors (5 V, 0.8 €). These motors can be easily operated with portable power banks (those used for cell phone charging). In fact, the commercial availability of solar chargers contributes to the portability of these devices.

Cost-effective SPs are also very relevant in this context since using fresh SPs avoids potential cross-contamination between samples. Several SPs (in the form of disks, membranes, and tapes) have been used in these devices. Borosilicate disks modified with carbon nanohorns were initially used as SPs. The porosity of the disks guaranteed a rapid extraction rate, but the synthesis of the disks (which were not commercially available) somewhat restricted the number of sampling locations. Considering this initial approach, commercial availability or synthetic affordability has been considered in the design of new SPs. Commercial nylon membranes, lab-made magnetic paper, and magnetic tapes containing commercial polymeric particulate sorbents have been applied successfully.

The miniaturization of the devices and the incorporation of open-source technologies (Arduino-controlled devices integrating sensors) are the latest trends in this research line. The main perspectives of this research line will be finally outlined, presenting new strategies for simplifying the analytical procedure.

Acknowledgements

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KN-06

Harnessing microextraction methodologies for the characterization of complex samples

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Keywords: *Microextraction, Complex samples, Biocompatible extraction phases, Environmental analysis, Bioanalysis*

The separation of small molecules from complex samples often poses the ultimate challenge to any analytical method development process, whether for targeted or non-targeted analysis.
Moreover, trends in the development of new microseparation techniques for extraction of small molecules have recently shifted toward greener and faster approaches, guaranteeing sustainability and high throughput of the extraction process. Solid-phase microextraction (SPME) complies with all the features above and provides simultaneous extraction/enrichment of the targeted analytes.
In this work new microextraction methodologies to probe the chemical composition of environmental and biological samples, and to assess the partition of small molecules in heterogeneous systems will be discussed. Various classes of environmental contaminants, namely PFAS, pesticides and pharmaceuticals were targeted in our work, and specialized extraction technologies were developed to guarantee their selective extraction and preconcentration from complex samples prior to analysis by gas-, liquid-chromatography and direct introduction to mass spectrometry. These methods become critical to assessing pollutants' environmental mobility and routes of exposure for living systems.
The use of biocompatible extraction phases and alternative SPME geometries will be also discussed to address specific analytical needs and guarantee minimal disturbance of partition equilibria during the extraction process.

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KN-07

Omics analysis of natural products is going greener: Opportunities from new materials combined with microextraction techniques

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Keywords: *Natural products, Deep eutectic solvents, Microextraction, Green sample preparation, Metrics*

Natural product analyses must cover a wide range of topics, from metabolomics studies to quality and safety controls. In all cases, sample preparation plays a fundamental role, as downstream analyses detect only metabolites previously extracted. On the other hand, quality control analyses require the determination of single or multiple metabolites, which are often present in trace amounts. Therefore, the choice of the correct extraction phase and technique is of paramount importance and the most critical parameter to be considered, also taking into account the complexity of the plant biological system.
Most studies and official methods for plant matrices still use traditional extraction techniques that have significant environmental impacts. However, there are new environmentally friendly alternatives that are more in line with the principles of Green Analytical Chemistry. For example, miniaturized techniques and new classes of more sustainable extraction phases that meet Green Analytical Chemistry criteria are increasingly being used. However, it is also important to keep in mind that accurate and reliable measurements are required, especially for industrial quality control laboratories that have to deal with a variety of norms and quality standards, and that practical considerations such as productivity, cost, and simplicity of methods should not be neglected.
This communication will explore, through a set of case studies in the natural product field, the possibility of improving the environmental footprint of sample preparation while maintaining appropriate analytical performance and laboratory productivity. With respect to extraction, particular emphasis is placed on the use of new and renewable materials. Indeed, plant products can be a source of effective solvents that can be used in conjunction with appropriate microextraction techniques for the isolation of target analytes, further improving the sustainability of the process. Moreover, the proposed methods are evaluated using different metric tools that can assess not only their environmental footprint but also their global performance.

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KN-08

Aptamer-based sorbents for the selective extraction of molecules and ions at trace levels in complex samples

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Keywords: *Aptamers, Selective extraction, Complex samples, Miniaturization*

The evolution of instrumentation in terms of separation and detection has allowed a real improvement in sensitivity and analysis time. However, the analysis of ultra-traces from complex samples often requires a purification and pre-concentration step before the analysis of the target analytes (organic molecules, ions) by powerful conventional instruments such as mass spectrometry coupled or not with chromatographic systems. In this context, extraction sorbents based on a molecular recognition mechanism appear as powerful tools for the selective extraction of a target analyte in order to obtain a more reliable and sensitive quantitative analysis.
One possible approach is the use of immunosorbents (ISs), based on the use of antibodies specific to the molecule of interest. Indeed, the high specificity and affinity of the antigen-antibody interactions allow selective cleaning of complex samples or extracts with high enrichment factors. This molecular recognition mechanism can also be generated by molecularly imprinted polymers (MIPs) whose synthesis leads to the formation of specific cavities mimicking the antibody recognition site. They have the advantage that they can be synthesized in a few days. On the other hand, their application to real samples requires a careful optimization of the extraction procedure to reach the expected selectivity.
An alternative is to use single strands of DNA or RNA, i.e. a specific oligonucleotide sequence, capable of binding to a given target analyte with the same affinity as antibodies. This sequence, called aptamer, can be grafted onto a solid sorbent and the resulting oligosorbent (OS) can be used for the selective extraction of different types of target analytes (toxins, pesticides, drugs, etc.) from complex samples such as biological fluids and food samples. Once the sequence is available, the development of an oligosorbent is less expensive than that of an IS and the associated extraction procedure is almost as easy to develop on OS as on IS, unlike MIPs.
Disposable SPE cartridges containing OS can be prepared and used as conventional SPE sorbents for processing various types of samples or extracts. The high selectivity provided by the extraction procedure may make their use particularly necessary when developing miniaturized devices due to the decrease in resolution that results from the use of shorter separation devices. In this context, a fully miniaturized analytical system has been developed for the quantitative analysis of target molecules in complex samples. Furthermore, if the potential of OS has been so far widely demonstrated for the extraction of organic compounds, their potential for the extraction of metal ions has been recently explored and applied to the purification of samples prior to ICP-MS analysis.

KN-09

Vacuum-assisted headspace microextraction: From theory to a new product

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Keywords: *Vacuum-assisted headspace microextraction, Fundamentals, Innovation*

The effect of vacuum sampling emerged as a new experimental parameter to control and exploit during headspace microextraction. The positive effect of reduced pressure sampling was initially reported for headspace solid-phase microextraction (Vac-HS-SPME), and the theoretical studies brought new insights on the processes underlying SPME sampling. At the same time, resulting methods were always found to yield high extraction efficiencies and very good sensitivities within short sampling times and at mild temperatures. The applicability of vacuum sampling was recently extended to microextraction methods that make use of high-capacity extraction phases, such as single-drop microextraction methodology, sorptive extraction using coated stir-bars marketed under the name, Twister™ and thin-film microextraction. This contribution also extends the applicability of the vacuum approach to SPME Arrow during the headspace sampling from honey samples. In all cases, conducting pre-equilibrium analyte sampling under vacuum resulted in a net improvement in extraction efficiency, and confirmed theoretical predictions stating that vacuum sampling not only accelerates the volatilization step but also analyte uptake by these high-capacity extraction phases.

The vacuum approach is disruptive by nature and over the past ten years an innovation strategy was adopted to transform the “theory” to a new product. In 2023, we were successful in the commercialization of a series of new such products and methods. This contribution succinctly reviews the most important theoretical formulations and experimental findings and relates them to the six stages of the product development process. Through this six-step plan the vacuum approach was taken from initial concept to final market launch. This transformation required the best of the traditions of science and innovation coupled with new emerging systems thinking and systems design. Catalyzing innovation in sample preparation is critical and inter-connected to research stimulation. More importantly, the commercialization of “safer” sample preparation products and approaches that reduce the environmental impact of analytical practices is directly related in delivering sustainability in sample preparation.

KN-10

Automation of sample treatment based on flow techniques for pharmaceutical development

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Keywords: *Automation, Drug development, Flow analysis*

Pharmaceutical development offers different challenges for analytical chemists. For instance, drug nanocarriers provide a means to modulate the solubility, stability, and delivery profile of pharmaceutical drugs. They afford new strategies for improving the therapeutic index of diverse drug molecules, often limited by bioavailability and/or toxicity issues, expanding the therapeutic opportunities for several health conditions. Recently, the growth of therapies based on biopharmaceuticals, namely monoclonal antibodies, have also contributed to a new demand for analytical methods that characterize different properties of these biological structures.

In this context, the present communication aims to highlight the importance and contribution of flow-based methods to support the pharmaceutical development, particularly the role of sample treatment. These methods have been established over the last few decades to automate (bio)chemical analysis while enhancing the figures of merit regarding accuracy, precision, and sample throughput. Dynamic in-vitro assays in pharmaceutical analysis such as permeation, release and dissolution tests have been employed with diverse aims towards quality control of pharmaceutical preparations. Particularly, assays based on Franz diffusion cell allows the study of transdermal permeation of free drugs and nanoparticle carriers loaded with active compounds. A flow-based system has been proposed to monitor the dermal permeation profile of lipidic nanoformulations containing caffeine using pig skin as surrogate [Talanta 146 (2016) 369-374]. Sample treatment steps, including online sampling and separation using a short, low-pressure C18 column were implemented in an automatic setup, allowing real time monitoring of a dynamic process, also providing reliable kinetic information needed to predict pharmacological outcomes.

Flow-based systems also encompass mesofluidic platforms, such as Lab-on-valve (LOV), that can handle both solutions and bead suspensions. Nanoparticles concentration directly impacts the dose delivered to target tissues by nanocarriers. The evaluation of this parameter is required during the developmental and quality control stages, for setting dose-response correlations and for evaluating the reproducibility of the manufacturing process. Recently, the automatic sampling and delivery of nanoparticles to the LOV detection unit were set by flow programming [Anal. Chem. 95 (2023) 4619−4626]. Nanoparticles concentration measurements were based on the decrease in the light transmitted to the detector due to light scattering, requiring only 2 min for each analysis. Measurements were performed on PEGylated poly-D,L-lactide-co-glycolide (PEG-PLGA) loaded with methotrexate and on polystyrene nanoparticles, with results comparable to particle tracking analysis (PTA). Finally, the potential for analysis of biopharmaceuticals is addressed, particularly using the bead injection approach to assemble immunoaffinity columns where antibodies can be captured and further handled, including direct on-column detection or elution for analysis by separative techniques.

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KN-11

Transition metal oxide-based sol-gel media for capillary microextraction

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Keywords: *Capillary microextraction, Transition metal oxide-based extraction media, Surface-bonded sol-gel coatings, Enrichment of biomolecules, Potential for environmental and biomedical analyses*

Sol-gel chemistry [C.J. Brinker and G.W. Scherer, Sol-gel Science, Academic Press, 1990; L. Klein et al., Eds., Handbook of Sol-gel Science and Technology, Vol. 1-4, Springer, 2018] provides a versatile pathway to covalently bind organic and inorganic moieties under extraordinarily mild reaction conditions (typically at room temperature). This offers new possibilities to fine tune extraction selectivity of sorbent media by manipulating the composition of sol-gel reaction components. We implemented this attractive feature of sol-gel chemistry and introduced sol-gel coated fibers in solid-phase microextraction (SPME) [Anal. Chem. 69 (1997) 3889–3898] and capillary microextraction (CME) [Anal. Chem. 74 (2002) 752–761]. Our initial work focused on the development of silica-based sol-gel extraction media for microextraction techniques. However, considering some inherent drawbacks of silica-based materials (e.g., poor stability under acidic and basic conditions), more recently we have initiated research projects focusing on transition metal oxide-based sol-gel extraction media [J. Chromatogr. A 1468 (2016) 23–32; J. Chromatogr. A 1522 (2017) 38–47; J. Sep. Sci. 41 (2018) 1663–1673; US Patent # 10967356B1 (2021); US Patent # 11344862B1 (2022)]. In this presentation, we will highlight our research efforts on the development of niobia-, tantala-, and other transition metal oxide-based hybrid organic-inorganic extraction media for CME in hyphenation with high-performance liquid chromatography (HPLC). Experimental details on sol-gel synthesis will be highlighted. CME-HPLC data will be presented to illustrate pH stability of the created transition metal oxide-based sol-gel CME coatings. High affinity of sol-gel niobia coatings toward phosphorylated compounds of biological and environmental interest will be demonstrated.

KN-12

3D-printed affinity and biomimetic sorptive phases: A new area of bioselective sorbents

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Keywords: *Bioselective extraction, 3D printing, Immunoaffinity, Biological membrane surrogate*

3D printing has made great strides over the last few years in various sub-disciplines of analytical science including micro/millifluidics, sensing and detection systems [Microchim. Acta 188 (2021) 265, TrAC Trends Anal. Chem. 136 (2021) 116177], yet recent focus has been geared toward exploiting its inherent merits for sample preparation and microextraction approaches [Anal. Chem. 91 (2019) 1140-1149, J. Sep. Sci. 43 (2020) 1854]. Efforts have been directed towards the exploitation of raw printable materials or blends thereof incorporating external (nano)materials as efficient sorptive phases in microextraction and separation techniques [Anal. Chim. Acta 1158 (2021) 338348, Anal. Chim. Acta 1185 (2021) 338796]. However, little research work has been focused on harnessing the potential of photopolymerisable acrylate-laden resins for immobilization of biomolecules for selective trapping of target species. This lecture aims at illustrating via representative examples the distinct synthetic routes for covalent immobilization of antibodies in tailor-made 3D-printed immunoaffinity stirring devices for microextraction of pharmaceuticals as examples of emerging contaminants in environmental samples and wastewaters [Microchim. Acta 189 (2022) 173]. We will also introduce an entirely new concept called biomimetic sorptive microextraction based on the immobilization of phospholipids for extraction of small organic molecules to serve as a relevant in-vitro bioparameter to elucidate supramolecular interactions with biological membranes, and thus predict the bioavailability/human oral absorption of target molecules as compared to in-vivo intestinal permeation. The role of 3D-printed stereolithographic platforms for immobilization of phospholipids and other membrane and plasma biomolecules will be described in details.

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KN-13

Microextraction techniques: A powerful tool for (bio)markers extraction in non-invasive diagnostic methodologies. Colorectal cancer as a real case

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Keywords: *Volatile organic compounds, Microextraction techniques, Diagnostic tests, Cancer diagnostics, Large intestine*

The human cells emit a variety of compounds in liquid and gas phase that can be measured in samples as blood, urine, breath, stool, etc. The compounds responsible of the odor are the volatile organic compounds (VOCs). These compounds are related with metabolic changes produced during processes such as cancer, necrosis or inflammation [Br. J. Cancer 103 (2010) 542-51]. Therefore, nowadays VOCs are being determined in different biological samples (i.e., urine, breath, feces) to study its correlation with some diseases.
Colorectal cancer (CRC) is a leading cause of mortality and morbidity worldwide, expected to cause 2.2 million new cases and 1.1 million deaths by 2030 [Gut 66 (2017) 683-91]. Early identification of CRC and detection and removal of advanced pre-malignant adenomas have been found to decrease CRC incidence and mortality [N. Engl. J. Med. 326 (1992) 658-62; Br. J. Surg. 89 (2002) 845-60]. Colonoscopy is the gold standard for the diagnosis of CRC, and fecal immunochemical test (FIT) is the most widely used non-invasive screening tool. Although FIT-based screening has led to a decrease in mortality, its performance is suboptimal, with a fairly good specificity but a high variation in sensitivity leading to misdiagnosis of CRC and unnecessary colonoscopy performance, using an important amount of resources [Eur. J. Cancer 37 (2001) 398-401]. Due to these limitations, there is a major need to develop new non-invasive and sensitive tools for early CRC diagnosis.
CRC is a disease in which the metabolites produced in the gut differed from a healthy patient mainly due to bacterial dysbiosis [Oncol. Rep. 35 (2016) 325-330]. It seems more and more evident than the gaseous constituents of the colon, which are mainly the metabolic byproducts of the colonic microbiota, are associated with the pathogenesis of colon diseases and can be modulated by drugs or diet. Due to the recent involvement and study of the microbiota in patients with CRC, the measurement of VOCs and gases from feces, among other samples, are receiving increasing interest due to these compounds are products of digestion and fermentation mediated by the intestinal microbiota including a complex interaction between colon cells, human fecal flora, mucosal integrity and invading pathogens. The evidence that bacterial cells and human cancer cells produce a different profile of VOCs due to a change in protein synthesis and metabolism is rising, that is why research in this topic has increased recently [Cancers 13 (2021) 2361].
The extraction of VOCs from fecal samples usually comprised a headspace technique in which the gas phase above the feces generated during warmed-up is directly injected in the GC-MS system [Colorectal Dis. 22 (2020) 1119-1129], or in which the VOCs are trapped in a sorbent disposed in the headspace that is later desorbed in the GC-MS system [Clin. Chim. Acta 542 (2023) 117273]. In this scenario, a sample preparation technique is a must in the stool samples treatment due to its complexity and trace levels of the target analytes. Therefore, solid-phase microextraction techniques are a powerful tool for the development of non-invasive diagnostic methodologies due to their high extraction efficiency, rapidity, solventless and environmentally-friendly character, among others.
Until now, few studies have been carried out searching for the potential of fecal VOC analysis for CRC detection with promising results [Cancers 13 (2021) 1820; Cancers 13 (2021) 2361]. Therefore, there is a necessity to develop sensitive methodologies for VOC determination in fecal samples in order to make them useful for CRC diagnosis and prevention.

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KN-14

Matrix solid-phase dispersion: From laboratory applications to pilot scale operation

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Keywords: *Matrix solid-phase dispersion, Petroleum biomarkers, Alkaloids*

Matrix solid-phase dispersion (MSPD) is an interesting, rather simple but versatile method for isolation of different compounds from both mineral (rocks, shale) or biological (e.g., plants, tissues, insects) matrices. The procedure is quick and effective, a very small solvent amount is required for the extraction. Extraction, concentration, and clean-up are combined in one step. MSPD possesses a wide range of applications in different areas of natural product chemistry, food, environmental, forensic, and petrochemical analysis. Typically, the extraction method optimization involves the selection of sorbent (e.g., silica, zeolites, sand, florisil) and of solvent used for analyte elution.
Several examples of the MSPD method will be shown, among them, the use of the zeolite adsorbents for selective isolation of saturated biomarkers ("molecular fossils" such as steranes, hopanes, tricyclic terpanes, etc.). The use of zeolites (ZSM-5) and sea sand resulted in very efficient and selective extraction of biomarkers from complex petroleum and rock shale mixtures. GC-MS/MS with triple quadruple configuration (MRM-acquisition mode) allowed unprecedented selectivity and sensitivity for biomarkers detection and identification. The MSPD method was compared with the traditional solvent extraction (Soxhlet) techniques.
Different applications of the MSPD method for alkaloid and polyphenolic compounds extraction will be discussed; for example, the analysis and monitoring of anti-inflammatory non-steroidal drugs (emerging contaminants) absorbed by aquatic plants. Tropane and pyrrolizidine alkaloids, as well as xanthines present in different insects after pollination of *Erythroxylum* spp. and coffee flowers, or after ingestion of toxic *Crotalaria* spp. plants were studied using MSPD method and GC/MS and LC/MS techniques. As the amount of biological material was very small (insects), MSPD method was the best isolation alternative for these biological compounds present at trace level.
The next application to discuss is related to the circular economy approach. Many agricultural procedures leave a huge amount of residual biomass, which can be used for bio composting, bio fuel, but more frequently as a waste. After steam distillation or hydrodistillation of aromatic plants more than 98-99% of residual biomass is left. We used this residual waste for polyphenol compounds isolation (flavonoids) using MSPD and SFE methods. For this purpose, the MSPD method was escalated, and the pilot plant was designed. The complete utilization of residual biomass was directed to the isolation of different biologically active phenolic compounds whose antioxidant properties were measured as an important variable for the MSPD process optimization. Scaling up the laboratory MSPD operation required the homogenization of solid sorbent and vegetable material in a single step with a ball mill, followed by elution and extract collection started with a solvent solid-suspension step in a cylindrical mixing chamber. A special sedimentation device was used for a liquid-solid separation. The resultant crude plant extract was concentrated by evaporation at low-pressure and spray-dried for microencapsulation. Several examples for different aromatic residual biomass use will be done. It was interesting to develop the process going from the laboratory application of MSPD method to the pilot MSPD equipment useful for the residual mass exploitation and added-value waste biomass process.

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KN-15

Recent advances and future trends in molecularly imprinted polymers-based sample preparation

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Keywords: *Molecular imprinting, Sample preparation, Binding sites, Water compatibility, Green chemistry*

Molecular imprinting technology is a well-stablished technique for the obtainment of tailor-made polymers, so called molecularly imprinted polymers, with a predetermined selectivity towards a target analyte or structurally related compounds. Accordingly, molecularly imprinted polymers are considered excellent materials for sample preparation providing unprecedented selectivity to analytical methods. However, the use of molecularly imprinted polymers in sample preparation still presents some shortcomings derived from the synthesis procedure itself limiting its general applicability. In this regard, molecularly imprinted polymers use to display binding sites heterogeneity and slow diffusion mass transfer of analytes to the imprinted sites affecting their overall performance. Besides, the performance of molecularly imprinted polymers in organic solvents is excellent, but their selective binding ability in aqueous media is considerably reduced. Accordingly, the present presentation pretends to provide an updated overview on the recent advances and trends of molecularly imprinted polymers-based extraction, focusing on those strategies proposed for the improvement of mass transfer and selective recognition in aqueous media. Besides, with the progressive implementation of Green Chemistry principles, the different steps, and strategies for the preparation of molecularly imprinted polymers are reviewed from a green perspective.

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KN-16

Micromotors in action as environmental micro-cleaners: Just a concept or a futuristic reality?

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Keywords: *Micromotors, Micro-cleaners, Water decontamination, Removal, Degradation*

High-quality potable water is a fundamental need for providing clean water to the entire population for human health, protecting the biodiversity of ecosystems, and preventing damage to the environment. Micromotors, or microscale devices capable of autonomous motion in solution, represent an emerging and attractive new approach as sustainable micro-cleaners in the field of environmental remediation. In this context, the utilization of self-propelled micromotors greatly enhances the efficiency of traditional operations due to their continuous movement improving the mixing of solutions and the speed of many chemical reactions and decontamination processes.
Autonomous micromotors can tailored be designed and functionalized with high-performing capabilities for pollutant degradation or removal. Their motion can be powered through the catalysis of chemical fuels, such as hydrogen peroxide or by external energy sources such as acoustic, light, and magnetic fields. Water decontamination mediated by autonomous micromotors is mainly focused on pollutant absorption and degradation mechanisms.
This Keynote will discuss selected micromotors-based assays with the potential for environmental remediation and future directions. In the first set of strategies, we will illustrate selected examples for the removal of inorganic pollutants through adsorption and Fenton-like processes [Environ. Sci. Nano 5 (2018) 2993–3003, Chem. Sci. 11 (2020) 132–140]. A second part of the keynote will be devoted to more sophisticated approaches for bacteria removal [Nanoscale 15 (2023) 9675–9683]. Ultimately, we try to answer the talk title's central and disturbing question.

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KN-17

Sustainable analytical strategies for multiresidue/multiclass monitoring of emerging risks in complex samples

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Keywords: *Capillary electrophoresis, Liquid chromatography, Cyanotoxins, Mycotoxins, Pesticides*

European Food Safety Authority (EFSA) defines an “emerging risk” to human, animal and/or plant health as a risk resulting from a newly identified hazard to which a significant exposure may occur or from an unexpected new or increased significant exposure and/or susceptibility to a known hazard. The successful identification of emerging risks in food, dietary supplements and waters is one of the main objectives for protecting public health. Therefore, advanced analytical tools are required for the detection and measurement of the indicator to be controlled, providing sensitive, selective, and accurate results. In this sense, we have proposed the study of some emerging risks, such as emerging mycotoxins, pesticide residues and cyanotoxins in different matrixes such as food, waters or nutraceuticals using sustainable analytical alternatives based on the use of liquid chromatography (LC) and electromigration techniques, such as capillary electrophoresis (CE), combined with efficient sample treatments. In these cases, the main difficulties in the development of the methods are the low concentration levels of the analytes, the complexity of the samples and the need to simultaneously determine compounds with different chemical properties.

The greenness of the proposed LC methods is based on the use of sub-2 micron columns requiring ultra high-pressure pumps, decreasing drastically the volumes of mobile phases, maintain very high resolution separations in shorter analysis times. A challenge today is to spread the use of CE, which can be considered as a sustainable technique in the field of liquid-phase separation science because of its miniaturized character, avoiding the use of organic solvents and requiring very low volumes of buffers and samples with minimum environmental impact, also taking into account the low cost of the silica capillaries in contrast to the price of chromatographic columns.

We present here some examples of sustainable analytical strategies based on the use of ultra-high performance liquid chromatography (UHPLC), hydrophilic interaction liquid chromatography (HILIC) or CE with different detection techniques and efficient sample treatments. In some cases, cleaner extracts are required, so solid-phase extraction (SPE) is the preferred option. A wide variety of sorbents is currently available, which can be combined in a tandem SPE to increase its versatility. This configuration was used in the multiclass determination of cyanotoxins with large differences in the polarity of the analytes, being possible their determination in reservoir waters, blue green algae dietary supplements and spinach. In other cases of multianalyte determination, generic extraction alternatives are preferable, such as the QuEChERS methodology, where the advantage lies in using medium-polarity solvents capable of performing extractions of a wide range of compounds with minimal cleanup, mainly compatible with MS detection. This option has been applied in the determination of emerging mycotoxins such as ergot alkaloids in nutraceuticals by UHPLC-MS/MS or enniatins and beauvericin by non-aqueous capillary electrophoresis (NACE)-MS/MS in cereals. A miniaturized QuEChERS method, with a reduced organic solvent volume and an increased preconcentration factor has been developed for the monitoring of neonicotinoids in pollen and honeybee samples by CE-MS/MS. Also, different strategies for the determination of the insecticide fipronil and its metabolites by LC or CE have been developed using a simple salting-out-assisted liquid-liquid extraction (SALLE) or liquid–liquid microextraction based on solidification of floating organic droplet (DLLME-SFO) with natural deep eutectic solvents (NADESs) as disperser solvents. These approaches have been applied in the determination of these residues in eggs and water samples.

Validation of these methods has been carried out according to the EU regulation, demonstrating that the proposed sustainable alternatives are fitted for purpose and could be applied in routine laboratories with satisfactory sensitivity and accuracy.

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KN-18

Challenges in extraction of aroma compounds from food matrices

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Keywords: *Food, Aroma, Matrix effects, Microextraction, Gas chromatography*

Odor-active molecules are characterized by two specific criteria: Each molecule exhibits its own odor threshold concentration as well as specific odor quality. The composition of odor-active compounds and their concentration in food products create the final aroma impression perceived by consumers. While in food products 10,000 different volatiles were detected, the group of compounds characterized as aroma-active comprises only around 200-300 of them. Odorants belong to various chemical classes, therefore they are characterized by different chemical properties, such as polarity or volatility. Additionally, the odor thresholds of potent odorants are usually very low, so their concentration in food matrices is usually also on a trace level. Due to these reasons, their analysis is a challenge for analytical chemists.

The most critical step in the analytical workflow remains the extraction. Many methods were invented and described until now in this area, however, the most popular ones are still exhaustive extraction, such as solvent-assisted flavor evaporation (SAFE), as well as green technology – solid-phase microextraction (SPME). However, some limitations of these methods were observed over the years, which lead to misinterpretation or confusing results occurred in the food analysis field.

In this talk, the problems and their possible solutions will be first demonstrated based on experiments with aroma compounds analyzed in different matrices, such as water or oil. Results from analysis by exhaustive extraction, as well as different forms of SPME (regular SPME fibers, overcoated SPME fibers, or novel form TF-SPME) will be demonstrated and discussed for headspace and direct extraction. In the further part, examples from complex food matrices will be shown. Analyses performed in alcoholic beverages (wine and beer) in relation to matrix influence on the quantitation of important odorants using SPME and TF-SPME will be discussed. Finally, problems with a non-homogenous solid matrix will be illustrated using cheese as an example. Various approaches in the quantitative analysis will be demonstrated for crucial aroma compounds, as well as a method based on TF-SPME will be presented to monitor cheese aroma development during storage.

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KN-19

Solid-phase microextraction and thin-film microextraction for direct and indirect characterization of organs' quality – A new avenue in transplant surgery

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Keywords: *Solid-phase microextraction, Metabolomics, Lipidomics, Mass spectrometry, Clinical analysis*

Solid-phase microextraction (SPME) and thin-film microextraction (TFME) are well known sampling, sample preparation and extraction methods. When SPME in its most common form of fiber provides a unique opportunity of performing in-vivo studies because of the small dimension of the probes and compatibility with various sterilization procedures, TFME is often used as set of coated blades arranged in 96-blade device therefore simultaneously increasing throughput and sensitivity of the analyses. There are number of works reporting utilization of SPME and TFME to quantitative targeted analyses as well as screening purposes or untargeted metabolomics or lipidomics studies. In the recent years SPME and TFME recorded a shift from more general bioanalysis towards pre-clinical studies on animal models and clinical studies involving smaller or larger cohorts of patients. In addition to therapeutic drug monitoring, untargeted profiling of metabolome and biomarkers discovery is of particular interest. With regards to medical areas, oncology and organ transplantation seem to be dominating.
In the talk, the use of SPME and TFME for assessment of quality of kidney and liver grafts will be presented. In direct analysis of organs, SPME fibers were inserted several times into the tissue, including the point before organ harvesting, during simulated time of ischemia, during preservation of grafts and finally, after transplantation. The restrictions related to the conditions in the operating room and the medical procedure itself had great impact on the final protocols. The optimization had to take into account short time of analysis, necessity of using sterilization method routinely used in the given hospital, coating length acceptable by the surgeons and enabling to obtain reproducible data considering heterogenous nature of the sampled organs. Additionally, in case of liver study, bile was selected for evaluation of changes occurring in the grafts subjected to static cold storage (SCS) or normothermic ex-vivo liver perfusion (NEVLP) collected during the peri-transplant period.
Contrary to direct organ sampling with SPME, bile studies with TFME gave more flexibility regarding time of extraction, coating length etc., but the specimen turned out to be challenging in terms of inter-sample reproducibility, high concentration of compounds, or high lipid content, just to name a few. The optimized protocols enabled to cover wide spectrum of polar metabolites as well as lipid species. Based on untargeted analysis, the differences between organs obtained from heart beating donors (HBD, i.e. no ischemia) and donors after cardiac death (DCD, i.e. subjected to different times of ischemia) as well as between organs subjected to different methods of preservation (cold vs. normothermic, mechanical vs. static) were reported. The most discriminating metabolites were proposed as potential biomarkers of monitoring grafts' function. For selected metabolites quantitative determination was performed.

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KN-20

Sustainable sample pretreatment for microplastic analysis in environmental samples

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Keywords: *Microplastics, Sample preparation, Flotation, Greenness assessment*

Identification and quantification of microplastics based on thermoanalytical and spectroscopic methods is one main part of assessing the fate of microplastics in the environment. However, the identification and quantification process is still challenging due to the often highly variable, dominant, and interfering matrix. Hence, a suitable sample preparation method is frequently required. In this context, often highly concentrated, expensive, and environmentally harmful chemicals are used. Following the goals of green analytical chemistry, which include the reduction of emissions and hazards to the environment and human health, these sample preparation methods should be modified or avoided, and more environmentally friendly methods should be developed. In this study the optimized hydrophobicity-water/air-based enrichment cell for microplastics (µSEP) is demonstrated, and its suitability as a sample preparation method for the determination of microplastics in soils is shown. The separation mechanism of µSEP is based on the hydrophobic adhesion of microplastics to finely dispersed upstreaming air bubbles. Therefore, for separation, only water and air are required to considerably reduce the matrix concerning microplastics analysis. Furthermore, commonly used sample preparation methods within microplastics analysis, such as electrostatic separation, solvent extraction, oil extraction, density separation, and an oxidative digestion using Fenton´s reagent, have been compared to µSEP and evaluated concerning their ecotoxicological impact by using the software tool AGREEprep. This tool has not yet been used concerning microplastics sample preparation methods. To that end, TED-GC-MS analysis showed the robustness and reproducibility of the optimized µSEP through the determination of recoveries. µRaman analysis indicate a high separation quality due to the possibility to perform a contrast-based particle identification and single particle measurements. Concerning the AGREEprep results, µSEP shows the best performance. Further, it has been noticed that metric tools like AGREEprep can provide a suitable overview about the ecotoxicological impact of different sample preparation methods, but its results can be influenced by the protocol chosen. However, this possible problem of subjectivity does not originate from the AGREEprep tool but rather from the lack of standardization. In addition, µSEP was successfully applied as part of a sample preparation method concerning the determination of atmospherically deposited microplastics in moss. Hence, the new microplasics and moss separation method, µMOS, is demonstrated in this study. Herein, a combination of exfoliation, sieving, and µSEP-flotation was used. This study shows the evaluation of µMOS through recovery experiments, its application to environmental samples, and a comparison in terms of data quality obtained by using µMOS and an oxidative digestion using Fenton´s reagent. As a result, suitable and robust recoveries can be achieved, synergies between TED-GC-MS and µRaman measurements are observable, and matrix interferences concerning TED-GC-MS and µRaman analysis can be minimized with the new µMOS method.

ORAL COMMUNICATIONS

O-01

Selective extraction of high-purity lignin from biomass with ternary deep eutectic solvents

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Keywords: *Selective extraction, Lignin, Biomass, Deep eutectic solvents*

In this study, we develop reusable acidic ternary deep eutectic solvents (TDES) made of alanine, lactic acid, and ethylene glycol for lignocellulosic biomass enhancement and lignin extraction. The required stabilization using diols prevented lignin condensation, and the selective separation produced lignin free of sulfur and silica. The delignification process and the structural alteration of lignin were characterized by nuclear magnetic resonance (NMR) spectroscopy. In addition to the primarily occurring demethoxylation and cleavage of the -O-4 linkage, lactic acid also caused the substructures to undergo acylation and oxidation. This produced lignin shows a desired molecular weight and monomeric yield (S/G ratio = 3.39), which is advantageous for use in reinforcement materials and bio-oils. Overall, the green TDES extraction technique may reveal fresh information on alternative pretreatments for sustainable biomass valorization.

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O-02

Adsorbent-assisted supercritical fluid extraction: A green process for the recovery of terpenoids with neuroprotective potential from olive oil agro-industrial waste

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Keywords: *Supercritical fluids, Adsorbent, Terpenoids, Neuroprotection, Alzheimer´s disease*

The residues generated during agro-industrial processing, as well as the food that is lost or wasted throughout the supply chain, constitute a huge socioeconomic problem and a strong environmental pressure on natural resources and the climate; therefore, the search for new bioactive compounds is an opportunity to revalue this biomass and take advantage of its richness in metabolites. Olive leaf is an abundant by-product generated by the olive oil industry and represents around of 25 percent of the total weight of solid waste. This biomass is characterized by a high content of phenolic compounds such as oleuropein with recognized therapeutic properties, but it also contains a minority group of terpenes with potential bioactivity. This research was oriented towards the valorization of the olive leaf through a green technique based on the supercritical fluid extraction coupled to adsorption process, in order to obtain a selective fractionation of different families of terpenoids with neuroprotective potential against Alzheimer´s disease. The dynamic extraction/adsorption procedure was carried out using CO_2 as solvent at 30 MPa, 60 °C, and times ranging from 0 to 120 min with different commercial low cost adsorbents. All fractions were chemically analized by gas chromatography coupled to quadrupole-time-of-flight mass spectrometry (GC-qTOF-MS), to obtain the terpenoids profile. As a result, triterpenoid-rich olive leave fractions obtained by using of silica-based materials, exhibited increased neuroprotection against some Alzheimer´s hallmarks, in terms of anticholinergic (AChE-BChE), antioxidant (ABTS) and anti-inflammatory (LOX) activities as well as the brain-blood barrier (BBB) permeability, among others. These findings demonstrated that this integrated sequential extraction/adsorption strategy was able to increase the bioactivity of the fractions, and thus their promising therapeutic effect against neurodegenerative disorders, due to a selective fractionation of terpenoids.

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O-03

Multiwalled carbon nanotubes embedded in a polymeric matrix as a new material for thin-film microextraction (TFME) of pesticides under different configurations: Suspended film and pipette tip

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Keywords: *Carbon nanotubes, Organic pollutant, Functionalized membranes, Thin-film microextraction*

The monitoring of organic pollutant in waters is mandatory to offer a control of the levels of some organic contaminants in environmental water bodies. Due to the low concentration levels, a preconcentration step is usually required before chromatographic analysis. For that, the development of new materials based on functionalized polymeric films is of interest. The materials under investigation are polymeric films based on cellulose triacetate (CTA) as the polymer and modified with multiwalled carbon nanotubes (MWCNTs). We have found that the presence of 10% (w/w) of MWCNTs in the film composition ensures an appropriate phase for the adsorption of pesticides: a fungicide (chlorpyrifos, CPS) and the bactericide triclosan (TCS) [Microchem. J. 175 (2021) 107120]. The thin-film microextraction (TFME) process is based on the direct contact of the film with the sample for the extraction of the analytes, followed by the elution of the loaded film using a small volume of the appropriate solvent. The new sorbents were applied under different configurations, TFME with the film suspended in the solution (S-TFME) and pipette-tip microextraction (DPX).

The characterization of the prepared films was performed using infrared spectroscopy (FT-IR) and scanning electronic microscopy (SEM). For S-TFME, the film area was 2 cm^2 and the film was fixed in the vial cap using a stainless-steel rod. For DPX, the pipette tips were prepared by placing a film piece of 2.9 cm^2 in the interior of the tip and held steady in position by means of glass wool. As for the parameters affecting the extraction, the main factors influencing the response were studied, taking into account the different configurations used: extraction time, number of strokes for the extraction and elution cycles, and the volume of sample solution. In this study, ethyl acetate was selected as elutant to recover the extracted compounds.

The extraction ability of the films was verified at different concentration levels of the compounds and a good correlation was found. Detection limits were determined at low $\mu g \cdot L^{-1}$ level. Parameters such as reproducibility and repeatability for the proposed film were found to be satisfactory with RSD ≤ 20% when using pieces from a single membrane.

Finally, the method was applied to real water samples, from two rivers in Catalonia (NE, Spain), namely Llémena and Osor River. The studied samples were spiked with the compounds to evaluate the matrix effect. Acceptable recovery values were obtained [Polymers 15 (2023) 314].

In conclusion, we have demonstrated that a polymeric matrix embedded with MWCNTs can be used as a new material for TFME of organic pollutants in natural waters. The different configurations tested gave satisfactory results, being the S-TFME superior in terms of sensitivity.

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O-04

A hydrophobic eutectic mixture as sustainable extraction solvent in LC-MS food analyses

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Keywords: *Hydrophobic eutectic solvent, Antioxidant solvent, Fat-soluble micronutrients, Pesticides, Dispersive liquid-liquid microextraction*

Eutectic solvents (ESs), both deep and ideal ones, represent a cutting-edge research topic in the field of Green Analytical Chemistry. In particular, hydrophobic mixtures are very interesting for extraction purposes, since in most cases the target analytes are characterized by quite high log P values despite being contained in aqueous samples. The green character of ESs depends on the natural and renewable source of their constituents, as well as on their negligible toxicity, flammability, and vapor pressure. On the other hand, this last aspect could limit their applicability in chromatographic analysis requiring specific conditions. Here, the hydrophobic eutectic mixture based on L-menthol and butylated hydroxytoluene in a molar ratio of 3:1 (MEN:BHT (3:1)) is presented and its application for the treatment of food samples is discussed, also in terms of compatibility with the LC-MS analysis. In particular, this eutectic mixture was successfully applied for the dispersive liquid-liquid microextraction (DLLME) of both fat-soluble micronutrients from commercial fruit juices [ACS Sustain. Chem. Eng. 24 (2021) 8170–8178] and pesticides from wine [Molecules 27 (2022) 908]. In the first case, it was found that this hydrophobic eutectic mixture matches perfectly with the non-aqueous reversed-phase chromatography-APCI-MS conditions, and its antioxidant activity is a plus value for the preservation of the easily oxidizable vitamins and carotenoids; in the application for the extraction of pesticides from wine, the reversed-phase chromatographic conditions combined with ESI-MS detection were carefully adapted to the hydrophobic extract, which was directly injected into the HPLC-MS system. In both applications the DLLME was performed by using ethanol as green dispersing solvent, especially for its role in keeping this ideal ES liquid even at low temperatures. In this regard, the useful alcoholic content of wine allowed one to minimize the solvent consumption as required by the Green Chemistry principles. The method, validated on a commercial fruit juice containing declared values of β-carotene and α-tocopherol acetate, was precise (4−8%) and accurate (4−6%); recoveries were ≥70%, while the detection limits were 0.05 $\mu g \cdot L^{-1}$ for β-carotene and 0.28 $\mu g \cdot L^{-1}$ for α-tocopherol acetate. As for the determination of 19 pesticides in wine, average recovery as high as 80%, precision between 3 and 14%, and limits of detection and quantification much lower than the maximum residue levels established by the EU regulation were obtained, making this multiresidue method fitted for the purpose.

O-05

New trends in sample preparation using 3D-printed devices

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Keywords: *3D printing, Sample preparation, Novel devices, Functional materials, 3D printed devices*

In the last years, 3D printing has been incorporated to many areas, especially in science fields such as Analytical Chemistry. In this sense, 3D printing in Analytical Chemistry, although is still an incipient technology, has been used for the preparation of detectors, electrodes and devices for sample preparation, among others. Fused deposition modelling (FDM), vat polymerization, photopolymer inkjet printing and selective laser sintering are the most typical 3D printing technologies, all with their advantages and weaknesses. All these technologies of 3D printing offer the possibility to fabricate novel 3D-printed structures, which cannot be easily created by other technologies or cannot be fabricated at low-cost. Therefore, 3D printing is an interesting alternative to take into account, particularly in sample preparation field. Nevertheless, FDM and vat polymerization has been converted in the most employed ones in sample preparation thanks to its low-cost, easiness and other specific merits, such as large availability of different materials (FDM) and high chemical stability (vat polymerization). In addition, the use of the low force stereolithography (vat polymerization mode based on the photopolymerization of a resin spot-by-spot and layer-by-layer) has shown interesting enhanced characteristics compared to other modes, such as the possibility to obtain highly transparent devices, high mechanical resistance and easy surface modification which provided a new alternative to combine with functional and/or selective materials such as metal organic frameworks, nanoparticles, and selective ligands, among others. Consequently, preparation of 3D-printed extraction systems for techniques based on solid-phase extraction (SPE) is a fascinating alternative to conventional supports.
In this communication, 3D printing current trends for novel devices development in both, sample preparation and detection will be discussed. Additionally, the characteristics offered by 3D printing technology which led to new ways to overcome sample preparation challenges, as well as their Green Chemistry viewpoint will be described. For this purpose, relevant examples that has been developed in CLECEM, 3D-MATEC and FI-TRACE groups will be selected to show the wide possibilities of 3D printing in sample preparation.

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O-06

Valve for flexible in-time SPE prior HPLC

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Keywords: *Online, Solid-phase extraction, Bead injection, Valve prototype*

Solid-phase extraction is the most used sample preparation technique. Manual processing supposes a huge workload for the analyst, and robotic stations resort to expensive hardware and consumables. Online cartridges are the greenest and most performant option, but they suffer from compaction and irreversible sorption of matrix components, and the sorbent chemistry and bed mass cannot be changed at real time. There is a need for an SPE that is renewable, flexible in terms of bed mass, sorbent chemistry and particle size, and that is online hyphenated to HPLC.

We present a new fluidic platform as add-on for liquid chromatography, that enables online “in-time” SPE in a renewable mode. The platform allows to select sorbent chemistry, mass, and particle size for every sample at real time and analyse it with different conditions if those are the workflow requirements. The used sorbent mass is in the range of 1 to 5 mg which offers a footprint greener than the manual or robotic station workflows and is washed from sample to sample with > 3000 column volumes of mobile phase. Thus, if the sorbent does not need to be exchanged, it can be reused for the whole batch.

The working principle is the unattended and pressure driven manipulation of bulk SPE sorbent inside a valve manifold under closed-loop conditions, so-called 'bead injection' (BI). A custom valve prototype was fabricated, allowing to park the sorbent in the injection loop of the HPLC and to remove it after the analysis with positive pressure. The fluid driver is a bidirectional pump working below 25 bars of pressure. Because of the simple hardware used for building the platform, it could be implemented in any autosampler of a commercial HPLC system.

The principle is presented using reversed-phase C_{18} and lipophilic/hydrophilic balance sorbents, as well as the comparison to a direct injection setup, including the automated optimization of the SPE workflow. The SPE bed can be quantitatively exchanged in 76 seconds; sample is loaded at 500 µL/min, thus providing high throughput for standard sample volumes below 100 µL, and enhancement factors > 200 for large volume injections (up to 3200 µL), circumventing the peak broadening.

For the first time, the unattended bead-injection manipulation of 5 µm sorbent for the SPE sample preparation has been evaluated, showing negligible Van deemter's C-term influence of the online SPE into the LC part. This data suggests that the herein presented platform can be downscaled to capillary LC. Furthermore, as an environmentally relevant proof of concept, the kinetics of a bioaccessibility extraction test of organic contaminants in soil were in-valve extracted and real-time monitored after a 30 µm-sized SPE.

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O-07

Carbon nanotubes-based membranes for disk-solid-phase extraction

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Keywords: *Solid-phase extraction, Membranes, Carbon nanotubes, Buckypaper, Environmental applications*

The development of ground-breaking materials with sorbent properties for solid-phase extraction (SPE) is one of most hectic research sectors of Analytical Chemistry. Among carbon nanomaterials, carbon nanotubes (CNTs) have some excellent properties that make them ideal candidates as sorbents for SPE. However, practical issues related to their handling (dispersion in the atmosphere, reduced adsorption capability due to bundling phenomena, sorbent loss in cartridge, etc.) have hindered their direct use for conventional SPE modes. Among the several solutions to circumvent such problems, there is the development of CNT-based membranes, such as buckypaper (BP). This is a free-standing paper-like material with a promising potential in the field of extraction science, which is still almost unexplored. BP is a highly porous membrane resulting from the aggregation of CNTs in a solid thin film with low specific weight and specific surface area (110 m^2/g) which is similar to that of microparticle carbonaceous sorbents, like graphitized carbon black (GCB) and porous graphitic carbon (PGC). However, compared with GBC and PGC, BP has a superior sorptive mass capacity due to the larger surface-to-volume ratio. Besides, its high permeability allows the direct treatment of samples from very complex matrices without clogging problems, which is a limitation of the classic SPE on cartridge. When used as a filter, the dynamic flow-through mode does not permit BP to achieve an adequate contact time with analytes, so its adsorption capability is not completely exploited. A completely different configuration has been conceived to favour the analyte adsorption by preparing different disk-SPE devices, useful to treat both environmental samples (stirring disk-SPE) and biological samples (rotating disk-SPE). Investigating the recovery dependence on the physicochemical properties of different classes of compounds, it has been observed that logP and pKa are two key parameters. In particular, compounds with pKa greater than 9 and log P between 2 to 4 have a greater probability of being adsorbed on BP, probably due to the hydrophobic interaction with its graphenic portion, while supplementary interactions such as hydrogen bonds and electrostatic interactions with the polar surface groups of the oxidized BP can improve the adsorption. Besides the improvement of the analytical figures of merit arising from a smart use of CNTs, the main practical advantages related to the employment of BP membranes are the great simplification of the SPE operations and the possibility of processing tens of samples simultaneously resorting to low-cost instrumentation (for instance a multiposition magnetic stirrer) and with a minimal effort of analysts.

O-08

Accurate and sensitive analysis of protein biomarkers at the intact and peptide map level by on-line aptamer affinity solid-phase extraction capillary electrophoresis-mass spectrometry

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Keywords: *Aptamer, Capillary electrophoresis, Mass spectrometry, Proteins, Solid-phase extraction*

Nowadays, capillary electrophoresis-mass spectrometry (CE-MS) is an excellent alternative to liquid chromatography-mass spectrometry (LC-MS) for the accurate analysis of proteins, at the intact level or after enzymatic digestion for bottom-up peptide mapping. However, one of the major drawbacks of CE-MS, and other microseparation techniques, are the poor concentration limits of detection due to the limited loading capacity needed for optimal separation at the microscale. Several strategies have been developed to improve CE-MS sensitivity, including on-line solid-phase extraction capillary electrophoresis-mass spectrometry (SPE-CE-MS) [Anal. Chim. Acta 1079 (2019) 1–19], which allows preconcentration and clean-up, after loading larger volumes of samples (hundreds of microliters in SPE-CE-MS vs tens of nanoliters in CE-MS). In this presentation, I will offer an overview of our latest developments in on-line aptamer-affinity solid-phase extraction capillary electrophoresis-mass spectrometry (AA-SPE-CE-MS) [Anal. Chem. 92 (2020) 1525–1533], which is a mode of SPE-CE-MS based on the great extraction capacity and selectivity of aptamers, as well as on their excellent compatibility with the specific requirements of the on-line electrophoretic separation and MS detection. I will present different applications for the analysis of protein biomarkers related to neurodegenerative and infectious diseases, and food allergy, at the intact level and from characteristic signatures of peptides fragments [Anal. Chem. 94 (2022) 6948–6956]. The combination of aptamer affinity, electrophoretic separation, and MS detection allows high-selectivity, high-sensitivity, and accurate quantification, with no possibility of false positives due to the unequivocal identification of the protein biomarker of interest.

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O-09

NH_3^+ modified SPIONs based extraction material for methotrexate study in pharmaceuticals nanodelivery systems

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Keywords: *Methotrexate, Extraction material, Nanodelivery system, Superparamagnetic iron oxide nanoparticles, Pharmaceuticals*

Advances in nanodelivery systems have led to a multidisciplinary research area for pharmaceuticals delivery in in-vitro and in-vivo studies. These systems are characterized by controlled, targeted and sustained compounds with biochemical activity. However, there are some important challenges that must be addressed such as toxicity control, biocompatibility, effective drug loading, targeting and release in the biological environment. From the analytical point of view, this has opened a wide range of opportunities from the development of extraction technologies to detection strategies. Hence, in the present work, a material based on superparamagnetic iron oxide nanoparticles (SPIONs) functionalized with amino groups (SPIONs-NH_3^+) has been proposed as sample preparation material for methotrexate (MTX) study. MTX is the widely used drug in cancer chemotherapy and is considered to be the first line drug of a number of rheumatic disorders [Front. Oncol. 9 (2019) 59; J. Sep. Sci. 45 (2022) 1153].
IR spectroscopy, z-potential and dHydro were used for material characterization after the SPIONs modification. The performance of SPIONs-NH_3^+ to retain MTX has been successfully demonstrated by using UV-vis spectroscopic measurements (LOD=0.3 mg·L^{-1}), RSD <2%) since quantitative extraction of MTX has been proved. The kinetic of that retention has demonstrated that low contact times were required. The results indicated that an ion exchange mechanism would be the explanation of this behavior taking into account the composition and potential interaction in the reaction media. Finally, MTX released from SPIONs-NH_3^+-MTX was also studied in cell media. Particularly, it was demonstrated that MTX can be delivered by an exchange mechanism, since MTX signal was recovered after the treatment of the abovementioned SPIONs. Therefore, these studies showed promising results in the extraction-release technologies for nanodelivery systems.

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O-10

Autonomous dried blood spot analysis by capillary electrophoresis

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Keywords: *Capillary electrophoresis, Dried blood spots, Automation, Drugs, Amino acids*

Dried blood spot (DBS) micro-sampling has been suggested as a viable alternative to the collection of venous blood and has attracted considerable attention in recent years because it offers numerous benefits to patients, clinicians, and analytical laboratory staff. Nevertheless, one of the major challenges in contemporary DBS analysis is DBS processing, which requires DBS transformation from a dry to a liquid sample and is usually performed manually. The manual processing involves the DBS punch-out from a sampling card and its elution, which are followed by centrifugation, evaporation, and reconstitution of the DBS eluate. Manual DBS processing is, therefore, tedious, labor- and time-intensive, and requires an additional manual transfer of the resulting eluate to an external analytical instrument for analysis. Obviously, there is an urgent quest for the development of simple and cheap solutions, which can offer fully unmanned DBS processing and analysis.

One such concept was recently presented in our laboratory and used a single off-the-shelf capillary electrophoresis (CE) instrument for executing all tasks of the analytical protocol. A typical commercial CE instrument contains two modules. The first module (consisting of a high-voltage power supply, detector, fused-silica (FS) capillary, and autosampler) is used for CE separation while the second module (consisting of a pressure system and air pump) for internal pneumatic liquid handling. The liquid handling module is connected with the CE autosampler through the FS capillary, and vials in the autosampler can autonomously be filled and their content homogenized by flushing various solutions and air, respectively, through the capillary. The same capillary can be subsequently used also for at-line injection, separation, and selective analysis of the resulting eluates by the first CE module. Thus, virtually any commercial CE instrument can act as an integral, automated system for continuous DBS elution, DBS eluate treatment, at-line injection of the resulting DBS eluate, and its quantitative analysis.

The actual lecture will summarize recent developments of the autonomous DBS analyses by CE achieved in our laboratory. These aimed at self-sampling exact volumes of capillary blood, reducing the volumes of the collected blood, using plastic vials compatible with CE autosampler for safe transport of DBSs, investigating and optimizing the FS capillary dimensions and CE parameters for rapid DBS elutions, programming continuous sequences for autonomous analyses of multiple DBS samples, using two interchangeable CE cartridges, and developing CE methods with various detection modes for rapid and sensitive determination of clinically important markers in DBSs. All DBS-related procedures (i.e. remote blood collection, blood drying, and DBS processing) were carried out directly in-vial and the resulting DBS eluates were at-line analyzed by CE. The proposed concept enabled high-throughput DBS analyses (several hundred DBS samples per day) and its suitability for clinical assays was exemplified by the determination of endogenous markers (amino acids, uric acid, creatinine) and exogenous species (warfarin, non-steroidal anti-inflammatory drugs) in remotely collected DBS samples.

The actual concept represents a progressive clinical tool for personalized medicine, screening populations at risk, and monitoring the effect of medical treatment on patients. It significantly improves the life quality of clinical subjects (no venous phlebotomy, no visits to medical centers) and clinical laboratory staff (no manual handling of biological materials and automated DBS processing/analysis), and can be useful in critical (e.g. pandemic) situations as well as it might propel a shift from the actual sick-care to a prevention-based healthcare system. Moreover, due to the universal character of the elution and the analytical procedures, the actual concept can be extended to the determination of a wide range of analytes in various dried material spots and might play a significant role in clinical, toxicological and forensic analysis in the future.

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O-11

Extraction of β-blockers from urine with a polymeric monolith modified with imidazolium ionic liquids in spin columns and paper

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Keywords: *Hybrid monoliths, Ionic liquids, Spin columns, Paper-based monolith extraction, β-Blockers*

A glycidyl methacrylate (GMA)-based monolith, modified with imidazolium-based ionic liquids (IL), was used as stationary phase for solid-phase extraction (SPE). The host monolithic support was prepared by in-situ UV polymerization in spin column and paper format. Two routes were developed for the incorporation of the IL into the polymeric monolithic matrix: in-situ generation of IL onto the GMA-based monolith, which was carried out with imidazolium ILs containing amine groups, and incorporation of the IL into the polymerization mixture, for which 1-allyl-3-methylimidazolium chloride was selected. The resulting sorbent materials were morphologically characterized by elemental analysis and scanning electronic microscopy (SEM), and used for the isolation of five β-blockers (acebutolol, alprenolol, carteolol, oxprenolol, and propranolol) from human urine samples. SPE in both spin column and paper formats reduced significantly environmental impact, costs and time in sample treatment. Also, the SPE devices can be reused (20 times) after a simple regeneration step. Under optimal conditions, β-blockers were quantitatively retained in the modified monolith, and desorbed with a water-methanol mixture, to be subsequently determined via HPLC with 15% (v/v) acetonitrile/10 mM IL, with UV detection. Both spin column and paper-based monolith extraction gave satisfactory limits of detection, and reproducibility usually below 8% (expressed as relative standard deviation). The novel phases were successfully applied to the extraction of β-blockers in urine samples with recoveries above 90%.

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O-12

Chromatography free screening and quantitation enabled through SPME DART-MS

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Keywords: *Solid-phase microextraction, Mass spectrometry, Environmental analysis, Food analysis*

In this short talk, we will present the principles and future work for the promising technologies combining direct ionization in real time with mass spectrometry, and different samples preparation devices based on SPME technologies, which enables the screening and quantitation of several compounds of environmental and food analysis interest. The advantages of the direct analysis is obvious for speed, easy of use but some challenges regarding sample matrix and complexity, will be overcome in the future combining appropriated sample preparation devices, and SPME is one of the most suitable technique. We will present the actual state of the art and the promising future trends in this interesting field of work.

O-13

Sample preparation strategies followed by GC×GC-based techniques for lipids investigation

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Keywords: *Lipids, Fatty acid methyl esters, Minor lipid components, Microwave extraction/derivatization, Preparative liquid chromatography*

Lipids, organic compounds containing hydrocarbon chains, are molecules essential for the structure and function of living cells. They comprise a wide range of structures, characterized by predominantly non-polar and hydrophobic molecular skeletons. However, some exhibit a slight polar or hydrophilic character, giving them amphiphilic properties. Lipids can provide useful information in different fields of chemistry such as the origin of and overall quality of a food product (food chemistry), the physiological state of an individual (clinical chemistry), and the quality of biodiesel (petrol chemistry).
Two-dimensional gas chromatography (GC×GC) methodology, combined with dedicated sample preparation techniques, has been applied to investigate different lipid fractions, namely total fatty acid profile and minor lipid components.
Total fatty acid methyl esters (FAMEs) were prepared using a single-step microwave-assisted extraction and derivatization coupled to a flow modulation GC×GC–flame ionization detector. The entire procedure was evaluated according to the AGREEprep metric for greenness and comparable with reference methods.
Minor lipid components, which represent between 1-5% of total lipid components, have been fractionated and focalized from the lipid matrix by preparative liquid chromatography before GC×GC-high resolution mass spectrometry investigation, leading to the identification of different chemical classes (e.g., intact fatty acids, fatty alcohol, sterols) that together can be considered as the fingerprint of a lipid sample.

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O-14

Microwave-assisted sample preparation in food analysis: A highly valuable ally

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Keywords: *Sample preparation, Food analysis, Microwave-assisted sample preparation, Microwave extraction*

Sample preparation is a routine, necessary step, but too often under-evaluated and consider as tedious and time consuming. The use of a properly optimized sample preparation procedure prevents contamination, improves accuracy, and minimizes the risk of results distortion.
The complexity of the food matrices often requires complex and time-consuming procedure, as for example, the step of saponification.
Microwave-assisted technology offers a reliable and efficient approach for sample preparation. Several processes can take advantages from microwave heating, reducing time and solvent volume involved, enabling the lab to have a greener and more cost-effective approach. In this presentation some examples will be discussed to highlight the benefits of using microwave-assisted sample preparation, such as better recoveries, lower extraction time, and combined step in the overall procedure. The examples will be on the extraction of contaminants (i.e., MOAH and MOSH), saponification and extraction of DAKs and sterols, and fatty acid methyl ester profile determination from foodstuff.

O-15

Determination of time-weighted average concentrations of volatile organic pollutants in the air based on solid-phase microextraction by a modified sampler with an alternative geometry

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Keywords: *Solid-phase microextraction, Time-weighted average concentration, Organic pollutants, Ambient air monitoring*

Determination of time-weighted average (TWA) concentrations is critical for pollutant monitoring in the air. The TWA concentrations are used to assess the total intake of air pollutants, health risks, and trends in air pollution levels. The most promising method for the determination of volatile organic compounds (VOCs) in ambient air, excluding the drawbacks of standard methods, is solid-phase microextraction (SPME). The determination of TWA concentrations by SPME is based on the extraction of analytes by the retracted SPME fiber according to first Fick's law. The retracted SPME fiber reduces the extraction rate, which is limited by the diffusion of analytes from a protecting needle tip to a fiber. At a constant diffusion rate, the sampling rate can be adjusted by changing the diffusion path length or the extraction time.

During extraction by retracted fiber, the metal surface of the protecting needle can adsorb analytes with possible saturation of the fiber tip, leading to insufficient accuracy. Tursumbayeva et al. proposed using a GC liner as a sampler, with exposed SPME fiber inside, to increase the accuracy of the determination of VOC TWA concentrations. The application of the liner excludes the possibility of analytes sorption on the metal surface during sampling. An increase in the inner diameter of the liner expands the working surface of the fiber coating. According to the COMSOL Multiphysics simulation, the use of a GC liner provides the same recovery as the fiber inside the protecting needle. However, it provides lower detection limits, due to the greater mass extracted.

To increase the accuracy of the determination of VOC TWA concentrations, a sampler with a new geometry has been proposed. Alternative sampler geometry increases the diameter of the extraction zone and decreases the diameter of the diffusion path. Modeling of the extraction process in COMSOL Multiphysics shows that the sampler with a new geometry should increase the accuracy to 88-91% compared to the retracted SPME and extraction in the liner (73-84%).

A gas generation system with known VOC concentrations was developed and used to produce stable analyte responses for over 48 h. The modified sampler was compared to the sampler proposed by Tursumbayeva et al. The modified sampler with Car/PDMS showed better recovery than the GC liner for 9 out of 13 VOCs, which varied from 91 to 137%. The use of MOF-199 with the modified sampler provides better recovery than the GC liner for all the studied analytes. The effect of the diffusion path length (Z=27, 67, 97, and 127 mm) on analyte recovery was studied. The lowest recoveries (23-69%) of the studied VOCs were obtained at Z=27 mm and the highest recoveries (56-116%) at Z=67 mm.

The developed method was compared with the sorbent tube-based method, which was used as the "reference" method. The sampling of real air samples in Almaty, Kazakhstan was conducted simultaneously by the sampler with alternative geometry and sorbent tubes. The TWA concentrations of VOCs determined by the developed sampler varied from 0.7 to 14.5 μg/m^3. The sorbent tubes showed lower TWA concentrations of the studied VOCs (0.07-7.5 μg/m^3).

Based on the obtained results, the developed SPME method in dynamic mode in combination with the proposed system can be recommended for the determination of the TWA concentrations of the studied VOCs with appropriate accuracy and reproducibility.

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O-16

Comprehensive investigation of different coatings and adsorbents for SPME and their influence on analytical performance

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Keywords: *Solid-phase microextraction, Adsorbents, Sample preparation*

Since its introduction in 1989 [Water Qual. Res. J. 24 (1989) 179–191], solid-phase microextraction (SPME) has gained a broad popularity in environmental and food analysis as well as many other application areas. SPME is a fast, sensitive, easy-to-automate and solvent-free microextraction technique which can be applied for various analytes in gaseous, liquid, or solid samples.
The stationary phases in SPME use either a polymer or a solid porous adsorbent embedded in a polymer. The various adsorbents have different ratios of macropores (diameters > 500 Å), mesopores (21-500 Å) and micropores (1-20 Å) which significantly impact their extraction capabilities. The fiber coating extracts analytes from the sample either by absorption for the pure polymer coatings or a combination of absorption and adsorption for the coatings with solid particles in the polymer. Over the years the technology evolved with the development of new coatings that increased extraction efficiency. Variables for the coatings comprise different adsorbents with their different properties, different polymers, the ratio of particles and polymer as well as simply the coating thickness.
In this work, different adsorbent materials, coating lengths and thicknesses have been comprehensively investigated to elucidate the impact of particle structure and properties and the coating dimensions on the extraction and desorption of a diverse set of analytes covering a broad range of molecular weights and polarities. Divinylbenzene particle coatings contain predominantly macro- and mesopores and are slightly less retentive compared to carbon adsorbents containing a higher share of micropores, which are providing better retention of small polar and, to a lesser degree, non-polar analytes. Larger dimensions (length, thickness) of the coating improve extraction capacity, but compromise desorption efficiency. The results of this work support SPME users in the selection of the best suited SPME phase for their analytical task.

O-17

On-site quantification of transformation products of unsymmetrical dimethylhydrazine in environmental samples using solid-phase microextraction and gas chromatography

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Keywords: *Solid-phase microextraction, Gas chromatography, Unsymmetrical dimethylhydrazine transformation products, On-site quantification, Accuracy*

Transformation products (TPs) of unsymmetrical dimethylhydrazine (UDMH) cause environmental and health risks, and their concentrations must be controlled in samples of soil, water, and air at the sites of rocket fuel spills and in possibly affected areas. Often, particularly after accidents, results of analyses are required as soon as possible after the UDMH spill for faster decision-making. In these cases, analyses should be done in the field using a portable instrument. Transportation of samples to a stationary laboratory can take many hours. During this process, some analytes can decompose in samples resulting in a major loss of accuracy. UDMH TPs can be determined on-site using a portable gas chromatograph (GC) or a GC with a mass spectrometric detector (GC-MS), which are commercially available. Solid-phase microextraction (SPME) can be used as an on-site sampling and sample preparation approach, which is very well-known for its simplicity, cost efficiency, and a possibility to achieve low detection limits. Methods based on SPME are available for the quantification of UDMH TPs in soil, water, and air using stationary GC-MS and GC with a nitrogen-phosphorus detector (NPD). However, these methods have not been optimized for on-site application, and their implementation needs additional research. This study was aimed at developing optimal procedures (calibration, sampling, sample preparation, quantification) for on-site quantification of UDMH TPs in samples of soil, water, and air using SPME and portable GC-NPD (chosen over GC-MS because of its much lower price).

For accurate on-site quantification of UDMH TPs in samples of soil using headspace (HS)-SPME, the greatest problem is the matrix effect. For achieving proper accuracy, existing methods use a combination of standard addition (SA) and internal standard (IS) calibrations, but this approach is not suitable for the field application because of substantial time expenses for analysis of a sample with several standard additions and equilibration of samples after introducing SA and IS. A simpler and faster approach is based on a preliminary extraction of UDMH TPs by water followed by HSSPME and quantification using external standard calibration. In this approach, HS-SPME can be conducted under vacuum (Vac-HS-SPME) for faster extraction and lower detection limits [Chem. Bull. Kaz. Nat. 89 (2018) 5–11]. Evacuation of samples in the field should not represent a technical challenge. On-site quantification of UDMH TPs in samples of water can also be conducted using Vac-HS-SPME and external standard calibration [J. Chromatogr. A 1555 (2018) 30–36].

For on-site quantification of UDMH TPs in air, three main approaches can be used: 1) extraction of analytes from a vessel with air sample (e.g., 20-mL vial or 250-mL gas sampling bulb); 2) purging air sample via cooled water followed by HS-SPME of analytes from a vial; 3) extraction of analytes from open air (protected from wind) by an exposed SPME fiber. The first approach [J. Sep. Sci. 45 (2022) 614–622] is the simplest, but it can be used only for analyzing relatively high concentrations of analytes in air, e.g., at the epicenter of UDMH spill, immediately after sampling (to avoid losses due to decomposition of analytes). Quantification can be conducted using an external standard calibration obtained by analyzing vessels filled with air spiked with different concentrations of analytes. The second approach is more complicated, but it can provide lower detection limits if optimized for capturing analytes from greater air volumes. In addition, it can be used to determine average concentrations over certain time periods (e.g., 1 h), which are required for estimating human health risks. Quantification of UDMH TPs in water with captured analytes can be conducted using Vac-HS-SPME and external standard calibration (as for water samples). The third approach is less studied, but it could provide the lowest detection limits with simplest sampling procedure and allows measuring time-weighted average concentrations. Optimization of such an approach for the greatest accuracy and lowest detection limits at fluctuating sampling conditions is possible using numerical modeling [Anal. Chim. Acta 1195 (2022) 339431]. Quantification using the third approach is possible using an external standard calibration obtained by introducing different masses of analytes into a GC column. Suggested approaches should be available for on-site quantification of UDMH TPs in air in different cases.

All approaches proposed in this abstract should be optimized for the chosen instrument and tested in the field.

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O-18

Paper-supported solvents as sustainable extractant phase

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Keywords: *Deep eutectic solvents, Microextraction, Paper-based sorptive phases, Environmental analysis, Biofluid analysis*

Paper is nowadays an essential substrate material for the development of a variety of analytical devices, including sensors, point-of-care single use strips or planar sorptive phases. Its physical configuration offers a high surface area with a reduced thickness, which ultimately increase extraction kinetics and efficiency. From the chemical nature point of view, paper consists of a highly packed cellulose fibers construct. The elevated number of hydroxyl groups on its structure provides a high wettability and intense H-bonding capacity to interact with analytes or modifying functional groups. Precisely, this characteristic can be used to modify its properties to create new sorptive phases for sample preparation. In such way, sustainable sorptive phases can be designed to accommodate a small amount of an extraction solvent, taking advantage of its interaction with the cellulose matrix. This communication proposes the use of paper coated with a traditional extraction solvent, such as 1-octanol embedded in the pores of commercial hydrophobic paper to enhance its interaction with opioid drugs in biofluid samples. In addition, regular cellulose paper can be used as support for a new class of green solvents, deep eutectic solvents (based on thymol-vanillin) by modifying its chemical behaviour thanks to the hydrogen bonding between the solvent components and the cellulose matrix. This new phase can be applied to the analysis of contaminants from environmental matrices. Both alternatives comprise a quick, synthesis-free extraction phase preparation based on sustainable materials. The simplicity of this phase preparation is key to minimize their overall environmental impact. Both extraction solvents can be physically deposited on the paper surface without the need of any chemical modification of the paper. The interaction of solvents and paper support allows the retention of the extractant phases during the microextraction process. In both approaches, analytes can be quantified using gas chromatography-mass spectrometry.

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O-19

A flower-shaped polymeric-coated cellulose paper for the isolation of organic contaminants from aqueous matrices

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Keywords: *Flower-shaped extraction unit, Recycled polymeric coating, Cellulose paper, Volatile organic compounds, Aqueous matrices*

In this communication, a new extractant phase based on a flower-shape modified cellulose paper is presented. Initially, the cellulose paper was cut into pieces of the optimized dimensions and coated with a thin layer of a polymeric phase. In order to increase the greenness of the procedure, recycled polymers were used as precursors. Next, two pieces of the polymer-coated cellulose paper were joined together by means of a pin in the shape of a flower. A triple rotator-motor device enables the simultaneous stirring of up to three extraction units.
The extraction system is simple and allows the automated stirring of the flower-shape extractant phase within the sample. Different polymeric coatings have been evaluated for the extraction of volatile compounds from aqueous matrices. The preparation of the polymeric coating is performed by simply dipping the piece of cellulose paper with the designed shape into a polymeric solution made from waste polymeric contaminants, minimizing the environmental impact of the synthesis. Also, the reusability of the extraction units was evaluated as it also contributes to increase the method sustainability.
This device configuration enables the analysis of sample volumes within the interval 10 to 100 mL. The extraction procedure was optimized by modifying the polymer type and percentage and the number of dips by using GC-MS. As the simultaneous extraction of hydrophobic compounds and their determination is considered a great challenge, the proposed device has potential to be applied in environmental and biological samples.

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O-20

The use of polymer inclusion membranes (PIMs) as sorbents for the preconcentration of antibiotics from natural waters

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Keywords: *Polymer inclusion membrane, Sulfonamides, Preconcentration, Speciation, Natural Water*

Nowadays, the presence of antibiotics in natural waters is of great concern due to the potential risks to public health and to the environment, in addition to the fact that they can induce bacterial resistance from their excessive use. In urban areas, wastewater treatment plants (WWTPs) cannot completely remove these organic pollutants, thus being released into different environmental compartments. Therefore, monitoring their presence in natural waters will be of paramount importance in order to improve the knowledge of their pathways of origin, transport, fate, and toxicity [Environ. Int. 140 (2020) 105733]. The relatively low levels of these organic compounds in aqueous media require a sample preconcentration before the chromatographic analysis. One of the most widely employed methods to perform this sample pretreatment is the use of solid-phase extraction (SPE). Nevertheless, when applied to complex matrixes, this technique can have poor recoveries and low reproducibility due to the interaction between the matrix components and the sorbent [Trac–Trends Anal. Chem. 80 (2016) 655–667]. For these reasons, this study presents the use of polymer inclusion membranes (PIMs) as an alternative to facilitate the monitoring of antibiotics in natural waters. PIMs are non-porous functionalized membranes made of a polymer, to provide mechanical strength, and an extractant, which is the responsible for binding/interacting with the target species [Anal. Chim. Acta 987 (2017) 1–14].

In our study, PIMs have been investigated as sorbent materials for the preconcentration of three antibiotics of the family of sulfonamides (SF): sulfathiazole (STZ), sulfamethazine (SMZ), and sulfamethoxazole (SMX) due to their widespread uses. PIMs were prepared using three different polymers (cellulose triacetate (CTA), poly(vinyl)chloride (PVC), and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP)) and two different ionic liquids anion-exchangers as extractants (trihexyltetradecylphosphonium chloride and methyltrioctylammonium chloride (Aliquat 336)).

Among the different membranes tested, it was found that the PIM made of 50% PVC and 50% trihexyltetradecylphosphonium chloride allowed a quantitative extraction for STZ, SMZ, and SMX (5 $mg \cdot L^{-1}$ each component, 25 mL water sample, membrane area 3 cm^2). The compound STZ exhibited the fastest extraction (quantitative extraction in 1 h), while SMX and SMZ needed 5 hours of contact. The fact that sulfonamides are extracted by an ion-exchanger reveals that these compounds are present as anions in the waters tested [Microchem. J. 124 (2016) 175–180].

The elution of the extracted compounds was also investigated using different organic solvents and procedures; the best results were obtained using methanol and no ultrasounds agitation was needed, obtaining an enrichment factor of 4.

The effect of the water matrix was also studied using different types of water, such as tap, bottled, and simulated natural water. It was found that the extraction of the antibiotics was not affected by the ions present in these matrices.

The ability of antibiotics to form complexes with divalent metal ions has been previously described. This is of great importance because these complexes are more persistent and toxic than parent compounds [Environ. Int. 157 (2021) 106863]. Hence, it is of paramount importance to provide analytical tools able to distinguish the existing species present in natural waters (free antibiotics and the metal-complexed ones). We have used the developed PIM for the preconcentration studies to investigate the effect of the metals Zn^{2+}, Cu^{2+}, and Ni^{2+} on sulfonamides extraction. We have found a decrease in SF enrichment factor for all the metals, being Zn^{2+} the metal that affected the most. These results show that antibiotics form complexes with metal ions, leading to species that cannot be extracted by the PIM. Therefore, the developed extraction system can be seen as a promising tool useful to perform complexation studies.

In conclusion, a simple and efficient sorbent based on a PIM has been developed to both preconcentrate and perform speciation studies of sulfonamides in water samples.

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O-21

AGREE and AGREEprep – Tools for greenness assessment in analytical chemistry

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Keywords: *Green analytical chemistry, Greenness metrics, Sample preparation*

Green analytical chemistry is a widely recognized concept, analysts more frequently implement these ideas during development of analytical procedures. It is a great challenge to develop tools for assessing greenness, due to the great number of assessment criteria and the contradiction of metric system objectives - the need to reflect the complexity of the criteria and the simplicity of presenting the assessment result.
Two tools have been proposed - AGREE and AGREEprep, which are used to assess the greenness of entire analytical procedures and sample preparation step, respectively. The developed tools were based on 12 and 10 impact categories, which were presented on a scale of 0-1, and applied to calculate the final assessment result. The evaluation criteria take into account, among others: selection and quantity of solvents, reagents, waste generation, energy consumption, sample size and analytical procedure time. The assessments are also based on the possibility of differentiation of the criteria significance by assigning them weights. Assessment procedures can be carried out using simple, intuitive software that allows users to generate a clear pictogram with information about the overall impact and structure of threats. The compiled version of the software can be obtained at https://mostwiedzy.pl/AGREE and https://mostwiedzy.pl/AGREEprep.

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O-22

Methods of analyzing biological material assessed using the WAC and ChlorTox Scale metric tools

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Keywords: *Green metrics, Forensic chemistry, Psychoactive substances, Biological samples, Green assessment*

The subject of this presentation is an overview of selected methods of sample preparation and analysis, in particular effective extraction techniques used for the isolation of psychoactive substances from biological materials used in toxicological-forensic analyzes. The process of preparing a sample for analysis is one of the first and critical stages of its analysis, which regardless of further phases of proceeding with the sample, determines the quality and reliability of the results of chemical analysis. This step is often time-consuming and requires the consumption of large quantities of reagents. The innovative such as: solid-phase microextraction and miniaturization allow not only to reduce their quantity, but also to perform the analysis using small amounts of the sample, which is often available in limited quantities in forensic analysis [Talanta 209 (2020) 120533; Anal. Bioanal. Chem. 414 (2022) 6355-6370]. One of the most important stages in the development of a new analytical method is its validation and assessment of greenness using the appropriate metric. In the present study, the White Analytical Chemistry (WAC) concept [TrAC-Trends Anal. Chem. 138 (2021) 116223] and the ChlorTox Scale [Green Anal. Chem., 2023, under review] were used to assess the methods of forensic and toxicological analysis from various angles. These tools turned out to be useful and reliable, allowing to easily compare and evaluate the different methodologies. The outcomes suggest which sample preparation methods seem globally the best (most white), and which are most green in respect to the total chemical risk related to the use of hazardous substances.

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O-23

33 years of SPME – A review from manufacturer's perspective

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Keywords: *Solid-phase microextraction*

SPME was invented by Janusz Pawliszyn of University of Waterloo in Waterloo, Ontario, Canada 33 years ago. Since that time, many scientists, researchers and users around the world have contributed greatly to the development and progression of the SPME technology.
This overview will cover milestone technological developments as well as some drawbacks that resulted in some learnings leading later to further improvements of SPME technology. Focus will be on the improvements in fiber technology (coatings, stationary phases, fiber cores, etc.) over the decades, on automation as a key parameter making SPME more popular and extension of SPME to solvent desorption and HPLC.

O-24

Sample preparation and GC×GC a powerful marriage in food analysis

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Keywords: *Multidimensional comprehensive gas chromatography, Food quality, Safety, Headspace extraction, Microwave-assisted extraction*

Food analysis is a rapidly evolving field moving towards more advanced analytical techniques to answer more complex questions and possibly respect the requirements of green and white analytical chemistry. Two general trends can be observed in analytical chemistry. On one side, sample preparation methods move towards more efficient, miniaturized, possibly solvent-free techniques; while looking at instrumental development, more powerful techniques are preferred to maximize the amount of information for every analysis. To reach this goal, the improvement can take place either at the chromatographic separation and the detector system. In this context, comprehensive 2D GC (GC×GC), invented by Phillips in 1991, is one of the most exciting and flexible techniques that can be used in food analysis. Nowadays, GC×GC can be considered a mature technique to be adopted as a routine food control technique for quality, authenticity, and safety assessment. The advantages mostly rely on the possibility of performing detailed and sensitive targeted and untargeted sample profiling contemporarily. Nevertheless, what is often undervalued is the synergic role that GC×GC and sample preparation can have together. On one side, the proper sample preparation can maximize the performance of GC×GC, bursting the information that the overall method can provide. On the other hand, the enhanced resolution obtained in GC×GC can simplify the sample preparation step, thus reducing manipulation, solvent consumption, and time.
In this presentation, the happy marriage between GC×GC and several different preparation methods will be described highlighting the mutual benefit. Examples related to food analysis both for quality and authenticity purposes and safety requirements, will be used, briefly describing the background related to the discussed topic. Alternative and novel approaches for headspace fingerprinting using high-concentration capacity tools (such as solid-phase microextraction) are presented, as well as the capability associated with the use of microwave-assisted extraction and liquid chromatography as sample preparation methods for very complex matrices.

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O-25

Development of green strategies for the extraction-encapsulation of antioxidant carotenoids from persimmon peels

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Keywords: *Carotenoids, Cyclodextrins, Extraction-encapsulation, Hydrophobic natural deep eutectic solvents, Persimmon peels*

The growing environmental concerns have increased the search for more sustainable processes, based on renewable raw materials to obtain food, energy, and chemicals. For instance, the food industry generates a large amount of waste, currently underused, which could be used as raw material for these purposes. That is why, this work was focused on increasing the value of waste from persimmon (*Diospyros kaki* Thunb.) peels, by obtaining bioactive lipidic compounds, such as carotenoids.
The extraction of carotenoids from natural matrices has been carried out by employing mainly toxic organic solvents. To replace these solvents, a new generation of more sustainable solvents known as natural deep eutectic solvents (NADESs) has been considered. NADESs present a great potential for extraction processes protecting the degradation of bioactive compounds as well as increasing extraction yields.
Therefore, in this work, a green extraction methodology using ultrasound-assisted extraction (UAE) and NADES was developed for the extraction of antioxidant carotenoids from persimmon peels. Seven NADESs were studied to select the best one to recover antioxidant carotenoids from this matrix. The antioxidant capacity and total carotenoid content of the extracts were evaluated. A Box-Behnken experimental design was used to optimize the molar ratio of the NADES components (1:1, 1:2, and 2:1), ultrasound amplitude (30-60%), and extraction time (3-15 min). Results showed that ultrasound amplitude and time had a positive effect on the extraction of carotenoids while the molar ratio of the NADES components had more effect on the antioxidant capacity of the extracts. The extracts obtained under the optimal extraction conditions were compared with those obtained under the same extraction conditions but using organic solvents instead of NADESs. The carotenoids present in the optimal extracts were determined by ultra-high performance liquid chromatography with a diode array detector (UHPLC-DAD). To recover the carotenoids from the extraction solvent, an encapsulation strategy based on the use of cyclodextrins was developed, which protects the bioactive carotenoids and improves their water solubility and their sustained compound releasing behavior. Three different cyclodextrins and different encapsulation times were tested, while the ratios of cyclodextrin-water and cyclodextrin-extract were optimized. Carotenoid-cyclodextrin powder was characterized by scanning electron microscopy (SEM) and Fourier transform infrared-attenuated total reflection (FTIR-ATR). In addition, the encapsulation efficiency and antioxidant capacity of the encapsulated were evaluated. Results showed for the first time that the use of hydrophobic NADES in combination with cyclodextrins could be a promising and sustainable alternative for the extraction-encapsulation of antioxidant carotenoids from persimmon peels.

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O-26

Simultaneous and sequential combination of orthogonal techniques for the sustainable and comprehensive extraction of proteins and polyphenols from malt rootlets

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Keywords: *Orthogonal extraction, Enzyme-assisted extraction, Microwave-assisted extraction, Ultrasound-assisted extraction, Pressurized liquid extraction*

The efficient and eco-friendly extraction of high added-value compounds from food waste is an important challenge in the 21st century. Nevertheless, conventional extraction techniques lead to low extraction rates and selectivity, require the use of polluting reagents and long extraction times, and, in many occasions, result in low quality compounds. Emerging technologies such as enzyme-assisted extraction (EAE), microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE), and pressurized liquid extraction (PLE) are sustainable alternatives to these techniques. However, in most cases, their single use does not guarantee the extraction of all target compounds from a sample. The combination of orthogonal techniques, based on different physical-chemical principles, could increase the final extraction capacity and be an interesting approach for obtaining high extraction yields. Additionally, combination of extraction techniques may improve the quality of the final product and reduce extraction times and environmental impact [Critical Rev. Food Sci. Nutr. 60 (2019) 1826].
This work proposes the development of sustainable methodologies using emerging techniques based on the use of polysaccharidase enzymes, MAE, UAE, and PLE for the holistic extraction of proteins and phenolic compounds from malt rootlets (MR), a protein-rich brewing waste (up to 35%). Box-Behnken experimental design was employed for the optimization of extraction conditions, in every case, using the proteins and phenolic compounds contents as response variables. Extracts were characterized by SEM, RP-HPLC, and SDS-PAGE. Results were compared with the obtained by the extraction of proteins and phenolic compounds using a conventional solid-liquid extraction under alkaline conditions. Eighteen commercial polysaccharidase preparations with different enzymatic composition were evaluated observing the best results with those containing cellulases. SEM images confirmed the release of intracellular compounds by single extraction techniques. Maximum extraction of proteins was obtained by PLE (67%) while the highest recovery of phenolic compounds was observed by UAE (1.74 g GAE/100 g MR). Since none single technique was able to extract all proteins from MR, different combinations of orthogonal techniques were investigated, simultaneously and/or sequentially, for a comprehensive extraction of these compounds. A 100% protein recovery was obtained by the sequential combination of UAE and PLE, while the maximum polyphenol content was observed by the combination of EAE with PLE (3 g GAE/100 g MR). This work demonstrates the potential of the combination of orthogonal extraction techniques for the recovery of high-added value compounds.

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O-27

Untargeted analysis of dairy products using vacuum-assisted techniques coupled with gas chromatography–mass spectrometry (GC–MS)

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Keywords: *Food science, Headspace, Sorptive extraction, Thermal desorption, Vacuum-assisted*

Determination of low-level volatile organic compounds (VOCs) is highly desirable in a plethora of scientific fields, ranging from food safety and quality, aroma, flavour and fragrance profiling, to environmental and clinical applications too. These compounds can provide many insights to samples in which they are contained. For example, perishable food commodities like dairy products produce malodours when not stored correctly or have passed their suggested shelf-life date, and so these unique compounds can be used as markers of quality. Extraction of volatiles is also beneficial in authenticity studies, determining geographical origin – in which unique markers can help determine areas of product growth, adulteration of premium products – whereby inexpensive yet similar alternatives are added to bulk the product, and identifying distinctive organoleptic (flavour and aroma) properties that top brands strive to achieve to stay on trend with consumers.

Compounds involved in formation of key aromas and flavours are alcohols, aldehydes, acids, esters, terpenes, pyrazines and furans, which can be present at low concentrations, so a technique that can extract low-level analytes is beneficial. Vacuum-assisted extraction is one such technique, in which a vial is evacuated of the headspace leading to a lower than ambient pressure within the vial. This promotes analytes that typically have low-affinity into the headspace of the vial. Extraction efficiency and sensitivity has shown to be improved, even when sampling at lower temperatures. It also allows for shorter sampling times as the headspace equilibrium is generated faster compared to ambient pressure sampling, reducing the energy intensity of the extraction and highlighting its potential as a ‘greener’ method. Implementation of the vacuum-assisted technology can be applied to a variety of techniques, including SPME fiber, SPME Arrow and headspace.

Here we present automated analysis of dairy products using the Centri platform. Sampled analytes were preconcentrated onto a multi-bed focusing trap, then subsequently backflushed in a reverse flow of carrier gas to the analytical column in a narrow band of vapour, producing sharp chromatographic peaks. The powerful combination of multiple sorbent and backflush operation allows a wide range of volatile and semi-volatile organics from every sample to be analysed in a single run.

Automated data mining and statistical analysis with ChromCompare+ shows several dairy products were easily distinguishable, while replicates of each type tight clustered, demonstrating good reproducibility. Vacuum assisted techniques were compared with non-vacuum techniques, and showed that when vacuum is applied, less-volatile compounds were present in higher abundances compared to ambient pressure samples, enabling more comprehensive sample information to be obtained.

O-28

A simple method for pesticide residues determination in green vegetables based on QuEChERS extraction technique coupled with GC-MS/MS and LC-MS/MS

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Keywords: *Food analysis, Matrix effect, Vegetables, Chlorophyll, Chromatographic analysis*

Nowadays, the use of pesticides is a very common practice to improve the yield and quality of agricultural crops. The use of pesticides undoubtedly has many benefits, as they allow increasing food production and helping reduce losses during food transport and storage. On the other hand, pesticides are one of the most dangerous groups of chemical compounds due to their toxic properties, environmental persistence and bioaccumulation capability. The overuse of these compounds combined with the lack of application of good agricultural practices can result in the presence of residues in the final products, thus, leading to potential health hazards for consumers. Ensuring food safety, developing analytical methods that allow the determination of wide range of pesticide residues is necessary. Consumer awareness of healthy food is constantly increasing, hence, in order to minimize risks associated with the consumption of foods containing pesticide residues, maximum residue limits (MRLs) have been established. The European Union in some cases has set MRLs at 0.01 mg/kg level and even at 0.005 mg/kg. Therefore, it is necessary to have reliable, sensitive, selective and accurate analytical methods to monitor the presence of different classes of pesticides in food matrices.

In the multiresidues pesticide analysis, green matrices represent problematic commodities due to the presence of large amounts of co-extractive such as chlorophyll in the extract. The co-extracted chlorophyll is a major issue in matrix interferences in pesticide residues analysis because of its non-volatile characteristics.

Nowadays, multiresidue method based on gas chromatography and liquid chromatography coupled with tandem mass spectrometry (GC–MS/MS and LC-MS/MS) is a required technique in routinely analysis because cover a broad scope of pesticides, due to effective separation, identification and quantification. A significant problem related to GC-MS/MS is its susceptibility to matrix interferences, which are known to affect quantitative performance, commonly known as matrix effect. One of the approach to eliminate or reduce matrix effects is reduction of matrix components by extensive clean-up. Therefore, the choice of appropriate sorbents for specific food materials plays a significant role in reducing chlorophyll and other pigments. The primary secondary amine (PSA) and octadecyl modified silica (C18) are most commonly using in d-SPE clean-up. However, the performance of these materials is not ideal for the treatment of complex matrix samples.

The aim of this study was to develop a multiresidue method that meets the SANTE/12682/2019 criteria for determination of pesticides by GC-MS/MS and LC-MS/MS in wide group of green vegetables simultaneously with reduced workload and ME.

In order to select the most suitable sorbents for chlorophyll extraction, two matrices with different chlorophyll content were selected: Chinese cabbage and spinach. In addition, ninety-four pesticides with different applications, chemical structure and polarity (from logP = -0.79 to 6.91) were selected to ensure pesticide recovery and matrix effect as required (SANTE/12682/2019). The optimization was evaluated by studying the recoveries at concentration level around 0.08 mg/kg in three replicates, which was added to each raw sample. The concentration of the fortification was selected to obtain reliable results for the conducted experiments. Matrix effect was studied using calibration curve in the range 0.05–0.14 µg/mL.

Due to higher degree of the purification extracts further studies were conducted using 900 mg $MgSO_4$, 300 mg C_{18} and ChloroFiltr mixture. The optimized analytical method for determination of over 400 pesticides in Chinese cabbage and spinach using GC-MS/MS and LC-MS/MS was validated. The performed validation confirms that the requirements of the SANTE/12682/2019 document have been met.

The developed methodology was applied for the determination of pesticide residues in 126 samples of green vegetables. The analysis were carried out in 2022 year, as a part of official testing of pesticide residues control in Polish crops. The tested samples belonged to the following groups: zucchini (7), kale (5), cabbage (1), dill (35), cucumber (63), leek (8) and lettuce (7). The 94 pesticide residues were detected in 57 vegetable samples. In 22 samples, the residues of active substances forbidden for use in specific crop were determined. It indicates that the wrong plant protection product usage is a significant problem. The exceedance of MRL was noted 4 times. There were 2 detections of chlorpyrifos and 1 detection of tetraconazole in the dill samples, 1 detection of linuron in the leek sample.

O-29

Study of derivatization conditions for determination of SCFAs by HS-SPME-GC/MS: Strengths and limitations

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Keywords: *Short chain fatty acids, Solid-phase microextraction, Derivatization, Gas chromatography, Metabolomics*

Volatile organic compounds (VOCs) are molecules characterized by presenting high volatility due to their elevated vapor pressure at ambient temperature. The analysis of these compounds is of major importance due to their relevance in human health, as many studies have found variations in their levels between healthy state and disease. Among these compounds, short chain fatty acids (SCFAs), those with fewer than 6 carbon atoms, are of great biological interest. They are involved in human metabolism, especially those produced by gut microbiota, participating in appetite regulation, energy production, glucose homeostasis, and immunomodulation. Additionally, these SCFAs also present important roles in the highly interconnected gut-brain axis, such as modulating neurotransmission, affecting the levels of neurotrophic factors, and participating in serotonin biosynthesis [Nat. Rev. Gastroenterol. Hepatol. 16 (2019) 461–478]. Although, headspace gas chromatography–mass spectrometry (HS-GC–MS) is widely considered the gold standard for VOCs analysis, the lack of pre-concentration of the technique may hinder HS's ability to detect compounds bearing lower Henry's Constant or present in lower concentrations. Because of their high polarity and volatility and their low concentration in biofluids, the determination of SCFAs is not an easy task. Conventional methods employ polar stationary phases in gas chromatography for the determination of native SCFAs, which presents considerable drawbacks. For this reason, most strategies for SCFAs determination by GC-MS employed derivatization prior to analysis. However, some of these derivatization protocols can be quite cumbersome, such as requiring anhydrous extracts, which difficult matters when handling biological samples. These protocols also employ high temperatures and long reaction times that may lead to the loss of the most volatile derivatives [D.R. Parkinson, Analytical Derivatization Techniques, vol. 2. Elsevier, 2012]. Chloroformate derivatization can be performed in aqueous media at room temperature, and it can be easily automatized with a robotic system. In this sense, this work presents a comprehensive study of chloroformate derivatization employing different reagents prior to extraction of SCFAs by HS-SPME. We combine the advantages provided by SPME, such as its ability to merge sample preparation, isolation, and enrichment into a single step, to reduce sample preparation time. Important to note that some derivatization protocols preceding HS-SPME for the analysis of SCFAs have been reported in the literature; however, these protocols often lead to the loss of the most volatile SCFAs, in special, formic acid. With this in mind, we optimize the derivatization protocol to achieve better sensitivity also for formic acid. In addition to the importance of greener sample preparation workflows, we optimize the usage of solvents during the derivatization step, in order not only to decrease organic solvent waste, searching for low-toxicity reagents, but also to minimize the possibility of displacement effects in the fiber coating due to the high concentration of solvents in the HS. In this sense, we investigate the utilization of PDMS-overcoated fibers [Anal. Chem. 89 (2017) 2978–2985] to inhibit the displacement phenomena and provide more accurate results. Sample stability, precision, and matrix effects were also investigated in human feces, urine, and plasma samples. Lastly, the results obtained by these chloroformate derivatization-HS-SPME-GC-MS protocols were compared to those obtained for HS-SPME-GC-MS analysis of underivatized SCFAs.

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O-30

Electromembrane microextraction (EME) of parabens and their main hydroxy metabolites in maternal urine and amniotic fluid

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Keywords: *Parabens, Electromembrane extraction, Maternal urine, Amniotic fluid, Mass spectrometry*

Parabens are a widespread group of endocrine disrupting compounds (EDCs), present in many personal care products, with confirmed affection to development and subsequently adult health. Pregnant women are considered one of the most vulnerable groups to these compounds due to transplacental passage that may have fatal consequences.
In this study, the simultaneously determination of 7 parabens (methyl, ethyl, propyl, isopropyl, butyl, isobutyl and benzyl) and two of their main hydroxybenzoic acids metabolites (4-hydroxy and 3,4,5-trihydroxy) is proposed. The optimized method was compatible with mass spectrometry detection and was applied in maternal urine and amniotic fluid samples obtained at delivery from pregnant women.
Sample treatment was performed by EME, a simple liquid-liquid microextraction technique based on the use of an electric potential to achieve a selective extraction across an organic solvent known as supported liquid membrane (SLM). Polypropylene hollow fibers were used as support for the organic solvent. Analytes were extracted using a three-phase configuration applying the following conditions: donor phase pH 4 (10 mL), acceptor phase pH 13 (50 µL), stirring rate 400 rpm, applied voltage 30 V, extraction time 40 minutes and 1-octanol as SLM.
Samples were analyzed by ultra-high performance liquid chromatography coupled to a triple quadrupole mass spectrometer (UPLC-TQ-XS, WatersTM) using a Zorbax XDB C_{18} column (150 mm × 3.0 mm i.d., 3.5 µm particle size) at 30 ºC. Mobile phase consisted of a mixture 5 mM ammonium acetate and methanol at a flow rate of 0.4 mL/min for 10 min under gradient elution. The detection was performed with negative ionization in an electrospray source at 1.5 kV capillary voltage, 150 ºC for source temperature and 650 ºC for desolvation temperature. Under these conditions, the method allowed limits of detection in the order of 0.1 ng/mL.

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O-31

Use of untargeted metabolomic to identify salivary biomarkers of Sjögren's syndrome

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Keywords: *Salivary metabolome, Biomarkers, Sjögren's syndrome*

Saliva is more and more considered as a source of biomarkers and recent advances in metabolomic, proteomic and genetic have allowed the identification and characterization of salivary components that may be useful for the diagnosis and monitoring of many diseases. The use of saliva is particularly interesting for the diagnosis of Sjögren's syndrome as this disease directly affects the salivary glands. However, the discrepancy in the metabolites described as having a differential expression with the Sjögren's syndrome questions the potential impact of saliva collection procedures, sample treatment and analytical methods used for the identification of potential biomarkers. Checking how the collection procedure affects the saliva composition is therefore crucial to ensure the reliability of the final results.

In order to achieve the most comprehensive analysis of the salivary metabolome, that may contain compounds belonging to a wide range of polarity and having various acidic and basic properties, four complementary LC-MS methods were optimized, RP-LC and HILIC were coupled to MS equipped with an electrospray source used both in positive and negative modes. The optimization was performed thanks to a mixture of 90 representative compounds (amino acids and derivatives, fatty acids, vitamins, steroid hormones, etc.) described in the literature as having differential expression in saliva in various pathologies and belonging to a wide range of molecular weight, pKa and polarity. Using these optimized methods, the three most frequently used sampling procedures were then compared (spitting, aspiration and Salivette® collection). The results demonstrated that spitting and aspiration gave statistically similar results for metabolites determination whereas the use of Salivette® gave lower concentrations for most compounds and was not adapted to a global untargeted metabolome analysis. The spitting and aspiration were thus kept for the untargeted metabolomics study.

As the Sjögren's syndrome is strongly associated with age and sex, the metabolic profiles of saliva samples from women affected by Sjögren's syndrome were then compared to those of healthy women of the same age group, which made it possible to identify 3 metabolites, alanine, isovaleric acid and succinic acid, with decreased concentrations in Sjögren's syndrome and which could serve as salivary biomarkers of this syndrome.

O-32

Determination of microplastics related pollutants in human organs

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Keywords: *Microplastics, Additives, Human organs, Headspace, Gas chromatography-mass spectrometry*

The increasing consumption of plastics has led to the generation of high volume of plastic waste whose environmental impact has been shown. Plastic particles below 5 mm, known as microplastics (MPs), are emerging pollutants which are also present in different environments as well as in organisms including humans. Exposure to MPs itself is a problem, and besides MPs can also be source of exposure to other associated compounds such as their additives (for example phthalates and organotin compounds) and monomers (like bisphenol A and styrene), which may cause adverse effects to human health.

MPs and their related compounds can enter the human body by contact, inhalation, and ingestion, the latter being the most common way of human exposure. The occurrence of MPs in human organs such as placenta, breast milk and lungs has already been demonstrated. However, the risk assessment of MPs' intake is still a global challenge for the scientific community, being a clear need of systematic studies in this topic.

In this communication, an analytical methodology based on headspace-gas chromatography-mass spectrometry (HS-GC-MS) has been developed to determine volatile compounds associated to the presence of MPs in human organs. Thirty standards, including plasticizers, monomers and other compounds related to plastic degradation, have been used for calibration purposes. The calibration curves were obtained by least-squares linear regression analysis of analyte peak area ratio with respect to the area provided by an internal standard versus analyte concentration. In addition, identification of other compounds (potential markers) present in the samples, which may be related to MPs pollution, has been evaluated by the usage of MS-dial software which applies a mathematical deconvolution approach to reassociate the precursor-fragment links and extracts structures using retention indexes (RI) and m/z data.

Different organs including lung, brain, heart, and liver were analyzed by incubating 4 g of the sample for 40 min at 130 ºC in the HS module and being automatically injected in the GC-MS system. Benzene derivatives and aldehydes have been detected in the samples, which may be indicators of MPs contamination. Potential differentiation of the samples regarding the pollutants content will be explored by using chemometrics.

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O-33

An improved miniaturized device to enhance the enrichment factors in liquid-phase microextraction: Application to the simultaneous extraction of polar and non-polar acids in biological samples

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Keywords: *Liquid-phase microextraction, Supported liquid membrane, Miniaturization, Sample treatment, Acidic drugs*

Liquid-phase microextraction has been successfully implemented as miniaturized systems in the last decade. The down-scale of that technique is becoming increasingly popular due to its advantages of low cost, low sample consumption and high selectivity compared to traditional set-ups. In this work, a new miniaturized device to enhance the enrichment factor in liquid-phase microextraction technique is proposed. The device was design for liquid-phase microextractions, and it was applied to the simultaneous extraction of acidic compounds from a wide range of polarity (0.5<log P<3). The device operated under stagnant acceptor phase conditions and all the operational parameters involved were optimized. Tributyl phosphate was found to be a new highly efficient supported liquid membrane to simultaneously extract analytes from very different polarity. The optimal donor and acceptor phase were pH 2 and pH 13, respectively. The donor flow rate and the extraction time were investigated simultaneously, offering great versatility with high enrichment factors (EFs). Limits of quantitation were within 0.02 and 0.09 $\mu g \cdot mL^{-1}$ for all compounds at 10 $\mu L \cdot min^{-1}$ as donor flow rate and 20 minutes extractions, offering EFs between 11-18 with only 200 µL sample volume consumption. The method was successfully applied in human urine samples, observing recoveries between 47-90% for all compounds. This new proposed system increases the wide range of applications, especially when the analytes are present in lower concentration in the sample.

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YOUNG ORAL COMMUNICATIONS

YO-01

Metal-organic frameworks-coated glass vials for analytical microextraction

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Keywords: *Metal-organic frameworks, In vial microextraction, Thin-film solid-phase microextraction, Coatings*

Metal-organic frameworks (MOFs) are crystalline materials formed by combining metal clusters with organic linkers through coordination bonds. They have permanent porosity and the highest surface areas known, as well as adequate mechanical and thermal stability. This set of properties makes MOFs interesting materials to be used as sorbents for the extraction and preconcentration of analytes in different samples. Indeed, there is a variety of microextraction modes that involve MOFs as extraction phases.
The use of immobilized MOFs onto support materials has proved to be a quite interesting approach for solid-phase microextraction (SPME) and also for thin-film solid-phase microextraction (TF-SPME), able to succeed in terms of analytical performance and also with green aspects considered.
With respect to SPME, MOF composites and neat MOF-based fiber coatings have been succesfully proposed, involving different strategies for their preparation. With respect to TF-SPME, mostly membranes involving mixed-matrix membranes based on MOFs have been developed. In such membranes, the MOF is acting as the core material responsible of the microextraction.
In this work, we propose an immobilization strategy via MOF in situ growth onto the inner walls of glass vials to produce a new TF-SPME device for analytical purposes. This TF-SPME approach using such MOF-based glass vials undoubtedly brings a remarkable simplicity to microextraction techniques, as simple stirring of the sample once added to the vial is required, followed by pouring (discarding) the sample, as the analytes are already trapped in the MOF coating attached to the inner walls of the glass vial. The proposed device offers fastness, reusability, as well as good analytical performance features, opening the door to simple on site analysis, with the added versatility of the MOFs.

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YO-02

Miniaturized magnetic-pipette tip microextraction: A new tool for microsample analysis

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Keywords: *Magnetic immunosorbent, Neonatal samples, Cortisol, Dispersive-based microextraction, Microsample*

The analysis of biological samples is usually challenging: Firstly, because of the complexity of the matrices that need a rigorous sample treatment and, secondly, because of the sample volume limitation to guarantee the health of the patient under study. This becomes especially struggling during the diagnosis of pathologies of critically ill patients and/or newborns, even more in those with a very low birth weight. Due to the fragility of these groups, the sample amount available is reduced drastically to a few microliters. In this regard, the development of analytical methodologies to handle low-volume samples is in demand.
In this regard, a miniaturized modification of our first prototype of magnetic-based pipette tip microextraction is presented as a sample preparation approach for microsamples. It involves a quick dispersion of a small amount of a magnetic sorbent material in a low-volume sample (10 µL) to entrap the target analytes. Next, the dispersion is aspirated using a (semi)automatic pipette through a pipette tip with a small cubic neodymium magnet inside, which retrieves the magnetic sorbent containing the analytes. After discarding the rest of the sample, the sorbent is properly rinsed by aspirating/dispensing deionized water, and then, the analytes are eluted by aspirating/dispensing an appropriate solvent.
This miniaturized approach was employed for the determination of free cortisol in serum and urine from very low birth weight preterm newborns, a vulnerable patient group who present low availability for sampling biological fluids. A magnetic immunosorbent made of a cortisol antibody was employed for the selective extraction, followed by liquid chromatography-tandem mass spectrometry. Good analytical features were obtained, such as limits of detection and quantification of 0.08 and 0.27 ng·mL^{-1}, respectively, linearity up to 50 ng·mL^{-1} ($R^2 > 0.999$), RSD values under 15% and relative recoveries between 91 and 111%. The cross-reactivity with other glucocorticoids (i.e., cortisone and prednisolone) was evaluated to show the selectivity of the extraction. Finally, the method applicability was demonstrated towards the determination of free cortisol in the serum and urine samples from low birth weight preterm newborns.
This new version does not only allow to work with lower sample volumes than the previous prototype, moreover, it adds several advantages such as: Avoiding the use of an external magnet and reduction of the desorption solvent volume increasing the green character of the method and comfort for the operator.

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YO-03

Sustainable gelatin-coated papers for the determination of steroid hormones in waters

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Keywords: *Paper-based sorbents, Microextraction, Estrone, Estradiol, Testosterone*

In this work, a simple, low-cost, eco-friendly, and effective sorbent based on the coating of cellulose papers with gelatin has been prepared. On the one hand, paper-based sorbents are cheap, versatile, non-toxic and easy to prepare. On the other hand, gelatin is one of the most interesting biomaterials because of its biocompatibility, high biodegradability, low-price, and high amount of hydroxyl, carboxyl and amino groups which allow its easy functionalization. Thus, gelatin is commonly used in several applications such as food, cosmetic, chemical engineering and pharmaceutical industries.
In this case, the main objective was the development of a sustainable, affordable and non-toxic hybrid material (paper modified with gelatin) with potential and innovative analytical applications. For that, different synthetic routes were evaluated selecting the most adequate and reproducible. It consisted of the following steps: 1) a cellulose paper is cut in a sphere shape with a diameter of 3 cm, 2) the paper is dipped into a glutaraldehyde solution for 10 s, 3) a solution of gelatin in water is pipetted onto the surface of the paper and, finally, 4) the obtained gel is cured overnight. Variables related to the synthesis procedure, such as the diameter of the paper, concentration of gelatin solution and amount of gelatin on the paper surface, were optimized. The extraction performance was evaluated using three steroid hormones (estrone, estradiol and testosterone). The variables affecting the extraction and elution of the analytes were also optimized. The prepared gelatin-coated papers showed a high affinity towards the hormones obtaining excellent preconcentration factors. Moreover, the modified papers were reused more than 6 times without decreasing the extraction performance, demonstrating thus the stability of the gelatin coating. Finally, the sustainable gelatin-coated papers were applied for the determination of the three target hormones in water samples.

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YO-04

Ionic liquids and surfactants as coating materials for iron oxide-based magnetic sorbents applied in the extraction of pharmaceuticals from biological samples

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Keywords: *Ionic liquids, Surfactants, Magnetic nanoparticles, Sample preparation, Pharmaceuticals*

Magnetic nanoparticles (MNPs) can be interesting approach in the sample pretreatment due to the large surface-to-volume ratio and the possibility of their easy removed using an external magnetic field, which significantly reduces the number of steps in the extraction procedure. In addition, they can be produced in any laboratory using a wide range of synthesis methods, in which the morphology of magnetic cores, and thus their sorption capacity, can be controlled by the selection of appropriate experimental conditions. However, obtaining the high extraction efficiency also requires the functionalization step, which by delivering the functional groups on the surface of magnetic sorbents affects the affinity of analytes to MNPs.
This contribution presents a comprehensive research utilizing different cation-anion combinations belonging to the group of ionic liquids (ILs) or surfactants in the functionalization of Fe_3O_4 MNPs. The influence of the cation, anion, length and amount of alkyl substituents in the tested coating materials on the extraction efficiency of the prepared sorbents is evaluated. The assessment also includes the results obtained for MNPs prepared with the use of various synthesis and functionalization procedures, which were coated with ten different ionic structures. In addition, the effect of ILs or surfactants forming the single or double layer – in combination with silica, commonly used in MNPs functionalization, is compared. Magnetic sorbents providing the highest extraction results are characterized using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetric analysis (TG) and transmission electron microscopy (TEM) techniques. Moreover, the potential of MNPs for development of sampling protocol for pharmaceuticals in biological matrices is demonstrated by their use in the extraction of epirubicin – anthracycline antibiotic applied in many chemotherapeutic regimens, from plasma and urine samples. The utility of functionalized MNPs is confirmed by the optimization and validation of MNPs-based method. In turn, the usefulness of the proposed method for therapeutic drug monitoring is proved by the results of analysis for samples collected from the pediatric cancer patient and presented in the form of epirubicin time-concentration profile in biological fluids.
The performed experiments allowed to classify ILs and surfactants as structures that can be used as coating materials for NPs and proved their potential as promising solution to overcome low extraction efficiency. Additionally, the designed protocol also pointed out the green aspect of the MNP-based sampling protocol. Due to the use of a small volume of matrices and sorbents and reduction of the consumption of harmful organic solvents, the application of IL/surfactant-based MNPs can be consider as eco-friendly approach in development of sample preparation procedures [Anal. Chem. 94 (2022) 16587–16595].

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YO-05

Synthesis and characterization of polystyrene-based sorbents for microextraction of selected psychoactive drugs from biological samples

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Keywords: *Electrospinning, Fibers, Solid-phase microextraction, Sorbents, Psychoactive substances*

The development of new sample preparation protocols based on solid-phase microextraction is increasing rapidly. This has an impact on more interest in the synthesis and characterization of new micro- and nanosorbent materials. The main goal of developing new sorbents is to improve the selectivity of the extraction process.
This work presents the preparation and characterization of polystyrene-based sorbents obtained by the electrospinning process for the extraction of selected psychoactive substances from biological samples. All fabricated sorbents were characterized by performing SEM images, measuring average fiber diameter, and examining their sorption properties. The fibers obtained from solutions with different concentrations of polystyrene in the range of 10.0 – 20.0 wt% were tested in case of use in solid-phase microextraction. In the next step, polystyrene fibers were blended with ZrO_2 particles and polyaniline to test the possibility of increasing the efficiency of the extraction process by using a blended sorbent. Among the tested materials, the sorbent based on polystyrene with polyaniline shows the best sorption properties of the tested substances. The selected sorbent was used in the extraction of a wide range of psychoactive substances (including ketamine, benzodiazepines, antidepressants, and cocaine) from biological samples such as urine and plasma. The precision of determinations in both materials indicated a high potential for the use of the tested sorbents in toxicological analyzes.

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YO-06

Headspace solid-phase microextraction as high throughput technique to extract potential urinary prostate cancer biomarkers. A metabolomic approach

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Keywords: *Metabolomics, Prostate cancer, Headspace solid-phase microextraction, Urine, Biomarkers*

Prostate cancer (PCa) is the second most frequent malignant tumour, the fifth leading cause of cancer death among men worldwide, and the most frequently diagnosed cancer in 105 of 185 of the world countries [CA Cancer J. Clin. 71 (2021) 209]. Advances in extraction techniques, chromatography, mass spectrometry instrumentation, and hyphenated systems make increasingly significant contributions to clinical applications, especially in cancer biomarker discovery and verification. The investigation of endogenous volatile organic metabolites (VOMs), which are produced by various metabolic pathways and present in several biofluids, such as plasma/serum, blood, tissue, and urine, is emerging as a novel, effective, and non-invasive source of information to establish the volatilomic biosignature of PCa. In this study, headspace solid-phase microextraction combined with gas chromatography-mass spectrometry (HS-SPME/GC-MS) was used to establish the urine volatilomic profile of PCa in order to identify VOMs able to discriminate the investigated groups. This non-invasive approach was applied to oncological patients (PCa group, n = 26) and cancer-free individuals (control group, n = 30), retrieving a total of 147 VOMs from various chemical families. This included terpenes, norisoprenoid, sesquiterpenes, phenolic, sulphur and furanic compounds, ketones, alcohols, esters, aldehydes, carboxylic acid, benzene and naphthalene derivatives, hydrocarbons and heterocyclic hydrocarbons. The data matrix was subjected to multivariate analysis, namely partial least-squares discriminant analysis (PLS-DA). Accordingly, this analysis showed that the group under study presented different volatomic profiles and suggested potential PCa biomarkers. Nevertheless, a larger cohort of samples is required to boost the predictability and accuracy of the statistical models developed.

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YO-07

Miniaturized QuEChERS combined with HPLC-MS/MS for determination of atropine and scopolamine in leafy vegetables

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Keywords: *Atropine, Scopolamine, MicroQuEChERS, Liquid chromatography, Mass spectrometry*

Tropane alkaloids (TAs) are a family of natural toxins with antimuscarinic effects produced as secondary metabolites. This family of toxins made up of more than 200 compounds produced by plants of the *Brassicaceae, Solanaceae, Convolvulaceae* and *Erythroxylaceae* families, among others [EFSA J. 2013]. The most representative compounds are atropine and scopolamine. These toxins can produce negative health consequences, if are consumed through contaminated food. The symptoms generated can vary depending on the dose from change in heart rate, excessive salivation, pupil dilation, reduced gastrointestinal tone, hallucinations to culminate in death at high concentrations.
The occurrence of TAs in vegetable food is consequence to contamination of crops with TA-producing plants. Atropine and scopolamine have been found in numerous foods such as cereals, aromatic herbs, honey, teas, but there is little information on leafy vegetables. Only one study demonstrated the presence of these compounds in spinach-based foods. For this reason, this work has focused on a rapid methodology framed in the principles of green chemistry to determine atropine and scopolamine from leafy vegetables. The methodology consisted of the miniaturization of the original QuEChERS (μ-QuEChERS) followed by liquid chromatography coupled to mass spectrometry (HPLC-MS/MS). The results showed low quantitation limits (≤2.3 ng/g), good accuracy (90-100%) and precision (RSD ≤13%) for both analytes. The method was applied to the analysis of TA-producing plants (*Brugmansia versicolor, Solandra maxima,* and *Convolvulus arvensis*) and eighteen samples of leafy vegetables. Of the samples analyzed, only three presented significant concentrations of atropine (2.7, 3.2, and 3.4 ng/g). The rest of the samples, 9 presented atropine and 1 presented scopolamine, in concentrations lower than the MQL.

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YO-08

A new microwave-assisted extraction technology for the profiling of free and esterified fatty acid in food matrices

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Keywords: *Microwave-assisted derivatization and extraction, Fatty acid methyl esters, Multidimensional comprehensive gas chromatography*

Microwave-assisted extraction (MAE) is a fast and efficient extraction technique based on the use of microwaves to heat the sample/solvent mixture to facilitate and improve the extraction of the analyte both in terms of efficiency and throughput. Several comparative studies have demonstrated the excellent performance, in terms of recovery and precision, obtainable with MAE compared to other traditional extraction techniques [Food Res. Int. 33 (2000) 733–741]. The main advantage is linked to the homogeneity and the rapidity of the heating process, which occurs inversely compared to a traditional heating process when polar compounds are present. The use of microwave technology can bring also other benefit, such as the possibility to merge different sample preparation steps in a unique process. Examples have been reported performing saponification and extraction simultaneously. In a previous work, we demonstrated the excellent performance in terms of accuracy and throughput of performing extraction and derivatization simultaneously in a procedure called microwave-assisted derivatization/extraction (MADE) [Adv. Sample Prep. 4 (2022) 100039]. The method was developed for characterizing the fatty acid profile of a large variety of food commodities.
In this work the potential of a new microwave technology was explored. This novel instrument in principle coupled the benefit of microwave technology with the use of high-pressure, which should, beyond increasing the boiling temperature of the extraction solvent, facilitate solvent penetration into the solid matrix, thus improving the overall performance of extraction. Moreover, the specific design of the novel system, consisting in a single chamber accommodating multiple vessels, allows for sample miniaturization. The potentiality of this synergic coupling of microwave and pressure have been investigated in the extraction and derivatization of fatty acids, comparing with the previous developed method. Moreover, a different procedure was developed by using dedicated experimental design to characterize free and esterified fatty acids present in hazelnuts, as marker of sample stability over time.
The obtained fatty acid methyl esters (FAMEs) have been characterized using multidimensional comprehensive gas chromatography (GC×GC) coupled to FID. Such a fully integrated platform represents a key platform for detailed large-scale screening in any lipid applications.

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YO-09

Ultra-high pressure supercritical fluid extraction (SFE) to obtain a terpenoids-purifed microalgae extract at semi-pilot scale

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Keywords: *Terpenes, Supercritical fluid extraction, Dunaliella salina, Bioactivity, Neuroprotection*

Dunaliella salina is a halophilic microalga well known for its ability of being capable to accumulate high amounts of β-carotene when cultured under specific growing conditions (high salinity). As a result, this strain retains a great commercial interest and potential. Moreover, different researches have related *D. salina* to diverse bioactivities, including antioxidant, anticholinergic and antihypertensive, among others. Because of that, its use in food, pharmaceutic and cosmetic industries has grown in the last years.

In this study, two different batches of *D. salina* were used to scale up and optimize a selective extraction process focused on the recovery of terpenes and carotenoids using supercritical fluid extraction (SFE) into a semi-pilot equipment (using a 2.5 L extraction cell and 400 g of microalga). In order to obtain the highest terpene content from these two batches, the extraction conditions whose optimum corresponded to 400 bar, 45 ºC and 2 hours with 60 $g \cdot min^{-1}$ of continuos CO_2 flow rate were optimized. Under these conditions, the obtained extract possessed a high amount of carotenoids, polyphenols and terpenes with high bioactivity levels in terms of antioxidant (ABTS and DPPH), anti-cholinesterase (AChE and BuChE), and anti-inflammatory (LOX) activities.

With the aim to evaluate the possibilities of this scaled-up process, an ultra-high pressure SFE was implemented, increasing the extraction pressure to 900 bar maintaining the rest of the optimized extraction conditions (temperature, time, and CO_2 flow rate) previously optimized at 400 bar. After the evaluation of the new process at 900 bar, the total extraction time could be reduced to 1 h. Although the total extraction yield decreased, the results of this new extract showed almost 10% higher activity than the optimum extract (400 bar) for AchE and BuChE inhibition, and more than 5% higher for LOX inhibition.

In order to explain the bioactivity differences between both extracts, the chemical characterization of both samples was performed. Quantitative results for total carotenoids, total chlorophylls, and total phenolic compounds showed that the extract obtained at 900 bar was richer in chlorophyll-a, carotenoids, and phenolic compounds than the 400 bar extract. LC-DAD-MS and GC-MS analyses were in agreement with these results; although the carotenoid profile was similar in both extracts, the overall carotenoid content of the extract obtained at 900 bar was incresed by a 60%. A similar trend was observed for the total terpene content, being the amount recovered at 900 bar, a 70% more concentrated in these compounds in comparison to the extract obtained at 400 bar.

These results demonstrate that the scale-up of *D. salina* SFE process to a semi-pilot step provides consistent results in agreement with our previous results obtained at lab scale. Moreover, this is the first report showing the usefulness of using ultra-high pressures during SFE for the extraction of bioactive compounds from *D. salina*. The use of the high pressure SFE process (900 bar) allowed to recover extracts with a higher concentration of the bioactive compounds resulting in a terpenoid-purified final extract.

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YO-10

Fiber-type *Cannabis sativa* L.: Innovative extraction methods for the analysis of the non-volatile fraction

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Keywords: *Natural products, Cannabis sativa L., Extraction phases, Microextraction, Liquid chromatography*

Environmental sustainability is currently a topic of global interest and regulatory organizations are developing policies to encourage the reduction of waste and pollution, and the efficient use of resources. In this sense, the valorization of plants as natural and eco-compatible resources and as reservoirs of bioactive compounds has become increasingly important for many applications, including pharmaceutical, cosmetic, functional food and food supplement industries. To avoid depleting endangered species and natural resources, multifunctional crops should be exploited at industrial scale. Fiber-type *Cannabis sativa* L. perfectly fits this purpose because it is widely distributed all over the world and can grow under versatile conditions. The interest for fiber-type hemp in the health field has gained much attention over the last years, being a source of a wide variety of specialized metabolites, that mainly belong to cannabinoids, phenols and terpenes chemical classes.
Several analytical methods have been proposed for the detection, identification, and quantification of phytochemicals from *C. sativa* plant. Due to the complexity of plant matrices, sample preparation is necessary to make the sample compatible with downstream analysis. The pre-treatment steps have a significant impact on the sustainability of the overall analysis process as they often require the use of disposable materials, energy-consuming equipment and instrumentation, and extraction methods that employ harmful solvents. The increasing demand for innovative technologies, energy saving, and greener solvents makes necessary the development of new extraction methods to obtain the metabolites of interest from natural resources.
In this regard, this study aims to present different lab-scale approaches for the extraction and enrichment of the non-volatile fraction of different hemp-related products (aerial parts, inflorescences, cannabidiol CBD oil). Innovative materials were tested as extraction phases in microextraction techniques and compared in terms of sustainability and analytical performances.

YO-11

Towards high throughput analysis using 96-well plate SPE for residue monitoring in food control

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Keywords: *Well-plate solid-phase extraction, High-throughput, Sedatives, Kidney, Chromatography-mass spectrometry*

The use of veterinary drugs in livestock animals may cause a risk to consumers. Actually, veterinary drugs are widely used in animal production to prevent for example infections, treat diseases and promote increases in feed conversion ratios. To ensure the safety of consumers, farmers must stop the administration of veterinary drugs before animals are slaughtered. Therefore, the European Commission established Maximum Residue Levels (MRL) for several veterinary drugs in a broad range of animal tissues. In modern farming, sedatives and β-blockers are frequently used to reduce stress during the transportation of food producing animals. Besides, to enhance the feed conversion ratio and consequently promote weight gain by reducing animal activity, sedatives are illicitly used in animal husbandry. The risk of residues in edible tissues is higher than other veterinary drugs because these sedatives and β-blockers are frequently used just a few hours before slaughter. Thus, to ensure citizens safety, in food control monitoring plans, every year up to 100 kidneys from different animals such as porcine, bovine and equine are analyzed.

Current methods to determine sedatives and β-blockers such as acepromazine, azaperol, azaperone, carazolol, chlorpromazine, haloperidol, propionylpromazine and xylazine consist of ion exchange solid-phase extraction (SPE) followed by their determination with liquid chromatography-tandem mass spectrometry (LC-MS/MS). However, this method is time-consuming and laborious, and requires a large consumption of solvents and consumables limiting the high-throughput of control laboratories. Hence, the miniaturization of SPE would permit us to get a faster, more automated, cost-effective, and greener extraction technique allowing a significant reduction in analysis time and solvent consumption that is required in food control laboratories.

This study developed a 96-well plate SPE method for the determination of sedatives and β-blockers in low volume of animal kidney. Based on extraction efficiencies, a comparison of different extraction solvents as well as the performance of the ion exchange 96-well plate SPE with different eluents has been carried out in both porcine and bovine kidney. Additionally, the LC-MS/MS method has been optimized to monitor target compounds with high selectivity and sensitivity in less than 9 minutes. Developed ion exchange 96-well plate SPE-LC-MS/MS method was validated based on Implementing Regulation (EU) 2021/808 performing full validation for porcine and partial validation for bovine, equine, sheep and goat kidney. In addition, how the use of matrix-matched calibration in porcine (most frequent sample to be analyzed) influences the determination of target compounds on the rest of the matrices was evaluated and it was observed that the performance characteristics were very similar allowing the application of a single matrix fortified calibration curve for the quantification of all animal species. The performance characteristics of the validation (1-5 $\mu g \cdot L^{-1}$) showed good linearity resulting in correlation coefficients (R^2) higher than 0.998 while decision limits (CCα) were between 1 and 1.2 $\mu g \cdot kg^{-1}$ in all cases. Besides, trueness and precision were determined at three levels (n=7) and the results showed values ranging from 85 to 103% and from 1 to 9%, respectively for all compounds.

The new developed method is simple, straightforward, has minimal solvent consumption and provides relatively high throughput suitable for food control monitoring. Additionally, a large benefit of the developed 96-well plate method is the potential for automation by using pipetting robots which can increase sample throughput and minimise the impact of human factor errors.

Acknowledgements

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YO-12

A green ionic liquid-based three-phase partitioning system as a simple miniaturized platform for the analysis of human saliva

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Keywords: *Human saliva, Ionic liquids, Preconcentration, Clean-up, Aqueous biphasic system*

The analysis of saliva has become a powerful tool to assess the human exposure of a wide variety of compounds with well recognized carcinogenic and endocrine-disrupting effects, including both persistence contaminants (like polycyclic aromatic hydrocarbons) and contaminants of emerging concerns (such as parabens, benzophenones, and bisphenols). The rising interest on saliva as bioanalytical matrix is linked to its simple, cost-effective, and non-invasive collection. Besides, as it is in direct contact with blood, it constitutes an alternative matrix to assess the blood levels of several contaminants without requiring an invasive sampling.
However, the salivary levels of contaminants are much lower than those found in blood or urine, and thus highly sensitive methods are required when dealing with the analysis of saliva. Furthermore, despite saliva is mainly composed by water, its protein content still constitutes a challenge, mainly when intending to directly couple the pretreatment of the sample with the analytical quantification instrument. In this sense, pretreatment steps (including centrifugation and deproteinization) followed by both liquid-phase microextraction (LPME) or solid-phase microextraction (SPME) approaches, in combination with highly sensitive analytical techniques (mainly LC or GC methods with mass spectrometry detection), are the strategies commonly reported. These approaches avoid damaging the analytical instrument with salivary proteins while ensuring adequate sensitivity in the determination. Nevertheless, these procedures are tedious and time-consuming, making quite desirable the development of more sustainable approaches for the salivary bioanalysis.
Aqueous biphasic systems (ABSs) are sustainable liquid platforms formed by mixing in water two water-soluble compounds that can be separated into two immiscible phases at certain concentrations and under specific conditions (in general, pH and/or temperature). ABSs are systems mostly based on water, thus constituting a greener alternative to conventional liquid-liquid extraction platforms based on the use of volatile organic solvents. Furthermore, these systems have benefited from the incorporation of ionic liquids (ILs) as phase-forming components. ILs are molten salts formed by the combination of bulky organic cations and organic or inorganic anions that have low vapor pressure at room temperature. ILs also show high solvation ability for a wide number of compounds, and high chemical and thermal stability. IL-based ABSs have been successfully applied for the pretreatment of serum and urine, mostly for the extraction and/or purification of proteins. Normally, IL-based ABSs perform as three-phase partitioning (TPP) systems when they are directly carried out in a biological sample with a high protein content. In those systems, a solid interphase (generally enriched in proteins) is formed between the two liquid phases of the IL-based ABS. This clearly expands the applicability of ABSs to integrated processes, in which extraction and purification can be accomplished in simple one-step procedures. Despite the greenness and efficient configuration of those TPP systems, they have never been used for the analysis of saliva.
In this study, a simple and integrated analytical method comprising simultaneously a clean-up and a microextraction-preconcentration strategy in human saliva is developed for the first time with ABS. The method is based on the use of a green IL-based ABS composed by the low cytotoxic butylguanidinium chloride (C_4Gu-Cl) IL and K_2HPO_4 as non-hazardous salting-out agent. This ABS successfully performs as a TPP system in human saliva. The system is applied for the microextraction and preconcentration of a group of bisphenols as representative emerging contaminants in saliva. The method avoids proteins (as they remain in the TPP interphase) and permits the direct combination with high-performance liquid chromatography (HPLC) and fluorescence detection (FD). The proposed setup avoids additional steps required for the removal of salivary proteins prior the analysis and successes with adequate preconcentration despite the use of a low volume of sample, thus constituting a step forward the simplicity and greenness of the methods for saliva analyses.

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YO-13

A magnetic deep eutectic solvent for dispersive liquid-liquid microextraction of bisphenols from food samples

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Keywords: *Magnetic deep eutectic solvents, Food samples, Liquid microextraction, Bisphenols*

Bisphenols (BPs) are commonly used in the production of thermal paper, epoxy resins, and polycarbonate plastics, which are used to make everyday things. These compounds suppose a risk to human health due to their ability to cause oxidative stress, mitochondrial dysfunction, poor inflammatory function and endocrine disrupting activity generating harmful effects on the endocrine, cardiovascular and immune systems, among others [Compr. Rev. Food Sci. Food Saf. 17 (2018) 1503]. These effects have been mainly related to bisphenol A (BPA). However, BPA-analogues may have the same or even more detrimental effects. One of the main exposure routes of people to BPs is through food and beverages stored in plastic recipients. Therefore, the presence of bisphenols in food samples must be controlled to ensure human health.

In order to develop a new methodology according to the principles of green analytical chemistry, the present work proposes the combination of miniaturized liquid-phase extraction techniques (LPME) for the separation and concentration of the target analytes (i.e., bisphenols) with the subsequent separation and detection by liquid chromatography-diode array detector (LC-DAD). Specifically, a vortex-assisted dispersive liquid-liquid microextraction (VA-DLLME) is performed, which allows to reduce the amount of reagents used, as well as the generation of waste. In addition, this study compares the use of a natural deep eutectic solvent (NADES) with the use of a magnetic deep eutectic solvent (MDES) as extractant in the microextraction process. Considering NADESs are made from two or more natural compounds, this enhances the ecological and sustainable nature of these solvents. On the other hand, MDESs are considered a subtype of deep eutectic solvents (DESs), with the novelty of containing a magnetic component. All these aspects make the use of MDESs of great interest in analytical applications.

In the current investigation, a hydrophilic MDES composed by choline chloride, ethylene glycol and iron(III) chloride (ClCh:EG:$FeCl_3$) in a molar ratio of 1:4:1; and a hydrophilic NADES (ChCl:EG) in a molar ratio 1:2 are used for the extraction of different bisphenols in food samples.

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YO-14

Use of aqueous biphasic systems to improve the analysis of cancer biomarkers

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Keywords: *Aqueous biphasic systems, Sample pretreatment, Human serum, Cancer biomarker*

Along the years, clinical care has been positively influenced by the analysis of biomarkers due to improvements in risk profiling, diagnostics, prognostics, and therapeutics of cancer. However, analysis is currently limited by the lower abundance of cancer biomarkers in biological samples as compared to other interfering molecules, which affects the performance of analytical techniques and, ultimately, leads to false positives/negatives. To deal with these analytical constraints, sample pretreatment is an essential task aiding analysis. In addition, analytical techniques able to feature an accurate, expedite and cost-effective detection/quantification are urgently required to broad the access to biomarker analysis and to meet the Green Analytical Chemistry prerequisites. In this framework, we have been using aqueous biphasic systems (ABS) as sample pretreatment strategies due to their enhanced biocompatibility, customizability, and practicability. The main advances achieved by us in the field of ABS for sample pretreatment, biomarker extraction and analysis are here overviewed and discussed. By placing our attention on protein cancer biomarkers and human serum samples, polymers, salts and/or ionic liquids (ILs) have been used as constituents of the ABS-mediated sample pretreatment approach. Efficient sample pretreatment and complete biomarker extraction are accomplished in a single step depending on the optimal selection of the ABS constituents. Furthermore, it has been shown that ABS-mediated sample pretreatment enables a more accurate detection/quantification of biomarkers by immunoassays. Overall, our results strengthen the role of ABS within the field of biomarker analysis, creating alternative Green Analytical Chemistry tools and, ultimately, improving cancer diagnostics and prognostics.

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YO-15

Evaluating new generations of magnetic ionic liquids as extraction platforms for organic compounds present in biological fluids

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Keywords: *Magnetic ionic liquids, Extraction solvents, Organic compounds, Analytical microextraction, Chromatography, Biological fluids*

Magnetic ionic liquids (MILs) are materials that have gained significant interest in analytical microextraction in the last years. These solvents present some of the typical properties of ionic liquids (ILs), including low vapor pressure at room temperature, low flammability, modulable viscosity and solubility, and impressive solvation properties for a wide variety of compounds. Furthermore, MILs behave as paramagnetic liquids. As a result of this impressive feature for a liquid material, the application of an external field to a MIL can serve to control the motion of the entire material, being possible its collection and isolation in a simple manner. Due to this ability to react or adapt to an external stimulus (the external magnetic field), MILs can be included within the group of smart materials.
Most of the MILs employed in analytical microextraction are based on metal anions such as tetrachloroferrate(III) combined with the typical organic cations of ILs (e.g., ammonium, phosphonium or imidazolium cations). However, these materials present drawbacks when are implemented in liquid-phase microextraction, including low stability in aqueous media, high viscosity, low extraction efficiency, and limited compatibility with chromatographic systems.
As alternatives, other generations of MILs have arisen in the last years. Among these new types of MILs, it is important to mention MILs based on metal cations, and bimetallic MILs. On one hand, MILs based on magnetic cations can undergo a metathesis reaction with different anions in aqueous media to generate water-non soluble MILs. This type of reaction can be performed *in-situ* during the microextraction method, favoring solvent manipulation and increasing the extraction efficiency. On the other hand, bimetallic MILs contain a metal-based component in either the cation and the anion and present higher magnetic susceptibility than previous generations of MILs.
The objective of this work is to gain insights about the behavior of novel MILs when implemented as extraction materials in analytical methods. Attention is paid to different aspects during all the steps of the analytical method: i) the stability of the MIL in the sample, ii) the integration of the MIL in the dispersive liquid-liquid microextraction method (selected as representative microextraction approach for MILs), and iii) their proper combination with either liquid chromatography and gas chromatography. Different analytical applications for the monitoring of organic compounds in biological fluids are presented.

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YO-16

Pore-networked membranes for the microextraction of personal care products and pharmaceuticals in environmental water

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Keywords: *Membrane, Metal-organic polyhedra, Microextraction, Personal care products, Environmental water*

The wide presence of pharmaceuticals and personal care products (PPCPs) in water is a major concern regarding current emerging pollution and urges their thorough monitoring in the environment to establish water quality standards [Anal. Chem. 94 (2022) 382]. Their detection at low concentration levels requires high preconcentration, which can be achieved by solid-phase microextraction techniques such as thin-film microextraction (TFME). Current commercial phases, including organic polymers and their composites with porous particles, lack selectivity and extraction capacity to meet the requirements of these analysis. Thus, mixed-matrix membranes (MMMs), which are composed of microporous adsorbents dispersed in the polymer matrix, are adequate candidates to overcome these issues [Chem. Rev. 120 (2020) 8378]. Numerous efforts have been devoted to optimizing MMM configuration and avoiding the undermining aggregation of adsorbents. However, most studies focus on gas separation and the peculiarities of liquid-phase applications, such as the slow diffusion and relatively big size of PPCP molecules, have not been considered when designing these membranes.
In this study, we show a new membrane configuration, so-called pore-networked membranes (PNMs), which presents two interpenetrated continuous phases: the interconnected microporous fillers and the polymer matrix. As a proof of concept, linked rhodium-organic cuboctahedra (RhMOPs) are chosen as filler materials because they can be linked by ditopic N-donor crosslinkers, leading to the formation of colloidal nanoparticles that interconnect to form colloidal gels [Chem. Sci. 10 (2019) 10833]. These features generate a continuous porous phase with relatively large extrinsic pores within the polymer matrix, which facilitates the diffusion and adsorption of the big PPCPs [Chem. Sci. 12 (2021) 12556]. By contrast to MMMs, PNMs showed surface homogeneity, enhanced stability and higher extraction capacity even in environmental water samples and at low filler loadings. Moreover, the PNMs exhibited extraction selectivity towards specific pharmaceutical drugs amongst 13 PPCPs, which can be easily tuned by selecting the adequate MOP and crosslinker to modulate the characteristics of the extrinsic pores. Further evaluation of PNMs in TFME allowed the detection of the target PPCPs at the nanogram per liter level in tap and river water samples.

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YO-17

Recycling of cellulose acetate from cigarette filters and its application in water treatment

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Keywords: *Cigarette filters, Cellulose acetate, Water treatment, Recycling, Sorbent materials*

One of the goals of green chemistry is the development and application of new sorbent materials with environmental friendly, low toxicity, recyclability and biodegradability characteristics. Several bio-based polymers, such as cellulose and cellulose acetate, are obtained from biomass or recycled waste. From this point of view, filters recovered from cigarette butts can be an important source of these two biopolymers, considering the fact that, worldwide, about 6 trillion cigarettes are smoked each year, producing between 340 and 680 million kilograms of waste.
With this in mind, this study aimed at: i) developing an effective procedure to recover cellulose acetate from cigarette butt filters; ii) using the recycled biopolymer to prepare a sorbent material to be used to remove organic contaminants from water.
The first phase of the work was focused on obtaining clean cellulose acetate from cigarette butt filters. It was accomplished by removing wrapping paper and unburned tobacco from the butts and subjecting the filters to washing with hot water and hot ethanol (non-solvents) in order to remove most of impurities, produced during cigarette burning. The efficacy of the cleaning was verified by characterizing the recovered polymer by UV spectroscopy, infrared spectroscopy (IR-ART) and thermal analysis (TGA, DSC), taking as a reference the pristine cellulose acetate of unsmoked cigarette filters.
The cleaned cellulose acetate was then used to make a composite sorbent with activated carbon having the characteristics of a cryogel. The synthesis took advantage by the sol-gel transition of the polymer solution. The recovered cellulose acetate was dissolved in a ternary solution of acetone/water/ammonia (60/40 v/v, 5 mM ammonia) at a concentration of 5% w/v to which 10% w/w activated carbon was added. The dispersion was shaken until a homogeneous solution was obtained and was allowed to gel overnight. The resulting gel (organogel) was then immersed in water to promote the transition of the dispersing solvent from organic to aqueous (hydrogel). The hydrogel was then frozen and freeze-dried until a porous cryogel was obtained. It was characterized by mechanical (compression) and thermal (TGA) analyses and morphological-structural analysis by IR-ART analysis, porosimetry and scanning electron microscopy (SEM).
The device was then applied to the adsorption of some organic contaminants from water. Such compounds were selected taking into account the different polarity, acidity, chemical structure and use (pesticides, pharmaceuticals, personal care products, etc.) so to be representative of the broad-spectrum removal capability of the material. Finally, through an experimental design, the best application conditions were determined in terms of treated water volume, minimum contact time and maximum concentration of pollutants.
The results have shown that this sorbent material holds out great promise in water treatment and that the proposed strategy is an effective way to recycle cellulose acetate from cigarette butts, which are in first place in the top-ten list of toxic waste.

YO-18

Lab in a bottle: An affordable and portable approach for environmental analysis

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Keywords: *On-site extraction, Portable, Affordable, Environmental waters, Phytoestrogens*

In this communication a new sampler based on open-source technologies for the on-site extraction of isoflavones from environmental samples is presented. The isolation of the target pollutant is carried out using a planar sorptive phase made up of commercial mixed-mode anionic exchange particles (MAX). The extraction unit was constructed using a double-side adhesive tape that was stirred in a vial containing the sorbent, and the MAX particles (ca. 6 mg) were adhered to the sticky surface. The device is wholly operated by an Arduino microcontroller that also integrates sensors (temperature and conductivity) to provide on-site information. To facilitate the functioning of the sampler, a cap of a glass bottle was adapted to host the extraction unit, the micromotor and the sensors.
For analytes extraction, a volume of 2.5 L of the water sample was placed in a bottle which was next closed by using the cap containing all the elements of the sampler. The extraction unit is stirred in the sample for a given time and then, it is withdrawn from the sample, dried with a tissue and introduced in a plastic bag for its delivery to the laboratory. Liquid chromatography coupled with mass spectrometry was selected as an instrumental technique. After optimization, the analytical method provided detection limits of 1.5 $ng \cdot L^{-1}$ (biochanin A and formononetin) and 15 $ng \cdot L^{-1}$ (daidzein and genistein). The precision, expressed as relative standard deviation, was evaluated at three concentration levels providing results better than 9.8%. The accuracy results support the application of the method. The device is cost-effective (ca. 16 €) and based on open-source technologies, thus permitting their easy reproduction. On-site extraction breaks with the classical analytical approach (based on sample transportation) and simplifies and cheapens the logistics. Also, it improves the stability of the analytes during storage, guaranteeing representativeness. The latter aspects are relevant since a single benchtop instrument (e.g., an official governmental laboratory) can analyze samples from different locations. This aspect is particularly critical in those places where expensive instrumentation is not readily available.

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YO-19

New developments in coated blade spray-mass spectrometry for high-throughput and rapid analysis

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Keywords: *Coated blade spray, Mass spectrometry, Solid-phase microextraction, High-throughput, Automation*

Coated blade spray coupled with mass spectrometry (CBS-MS) combines solid-phase microextraction's (SPME) efficient sample clean-up and enrichment and ambient MS's fast analysis and has proven to be an appealing alternative tool for the fast screening of target analytes in complex matrices. Herein, we focus on two important technical developments regarding CBS-MS including: 1) Analysis in both positive/negative modes using single blade; 2) Improving negative electrospray ionization (ESI) in CBS-MS by using a blade with barrier design.

High-throughput screening and quantitation of large numbers of compounds, especially in omics analysis, requires the use of both positive and negative modes in ESI-MS [J. Am. Soc. Mass Spectrom. 33 (2022) 1187–1193]. For realizing the polarity switching using single blade, three different strategies were proposed including: 1) One side of the blade for positive mode, and the other for negative mode; 2) Separating the ESI to two segment and applying negative and positive mode in sequential; 3) Real time polarity switching on the ESI source. From the results, all the above three strategies showed ideal reproducibility and have different features and advantages. Among them, the first strategy showed the best overall sensitivity as the desorption solvents for positive mode and negative mode can be optimized and applied separately on different sides of the blades. By using this strategy, high-throughput SPME was coupled with CBS-MS for the rapid analysis of 20 drugs of abuse in saliva samples in both positive and negative mode. The proposed method provided LODs between 0.005-10 ng/mL, with $R^2 \geq 0.9925$, accuracy between 72 and 126%, and RSD% < 15% for all three validation concentration levels.

Substrate-based ESI techniques like paper, wooden tip, plastic tip, and metal-needle-based spray suffer from corona discharge, high background noise, and unstable spray in negative ionization mode, especially for the analysis of complex biological matrices, such as blood and urine. We developed a new CBS design that features a barrier at the far end of the ESI tip [Anal. Chem. 94 (2022) 15879–15886]. The findings of this work show that the addition of this simple barrier enabled the total RSD% to be reduced to less than 10% for sample preparation, ionization, and the MS detection of several drugs of abuse in negative mode, without compensation using internal standards. The improved stability of ESI in negative mode was investigated by observing the ESI process with a micro-camera and testing via CBS-MS. The new design was applied for the analysis of three drugs of abuse in urine, with the calibration curve correlation coefficient ($R^2 \geq 0.9997$) being calculated without the use of internal standards. The overall RSD% of the peak area for one compound in 42 samples was 6.9%, which highlights the method's incredible reproducibility compared to other ambient MS techniques for analyzing real samples. The CBS device with a barrier was also applied for the on-blade sampling of 14 drugs of abuse in 20 µL of plasma spot in positive ionization mode. The results of these tests yielded a calibration curve correlation coefficient of $R^2 \geq 0.9883$ and limits of quantification (LOQ) between 0.25-25 ng/mL. The obtained results provide guidance on CBS device design optimization and the effective automation of the protocol.

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YO-20

Development of SPE-CE methods for the determination of active pharmaceuticals ingredients in an industrial manufacturer's wastewater

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Keywords: *Solid-phase extraction, Capillary electrophoresis, Active pharmaceutical ingredients, Pharmaceutical pollution, Wastewater*

Reducing manufacturing environmental pollution and promoting green chemistry and sustainability are top priorities for pharmaceutical manufacturers across the globe. To ensure the health and well-being of the environment, standard operating procedures (SOPs) are in place for air emissions and organic and biological waste in wastewater. While these emissions are regularly monitored, a significant water pollutant has been overlooked: pharmaceutical pollution. According to the World Health Organization, wastewater effluents constitute a substantial source of pharmaceutical pollution in environmental waters. Pharmaceutical pollution can have irreversible effects on the ecosystem, impacting the aquatic organisms that inhabit the ecosystem. Removing active pharmaceutical ingredients (APIs) from wastewater during the wastewater treatment process has proven difficult due to their chemical structures; therefore, more research is required. Detecting the APIs in effluents and ensuring that they are at a safe concentration before being released into the environment is of utmost importance. Research has shown that high-performance liquid chromatography (HPLC) has provided excellent results in this area, but there is one major drawback: it requires a large amount of organic solvent. Capillary electrophoresis (CE) is now being used as a greener alternative to HPLC as it requires little to no organic solvent, smaller sample volumes and provides faster analysis. CE is known for its poor sensitivity, so a pre-concentration step such as solid-phase extraction (SPE) can be used to improve the sensitivity of the CE. This research is a collaboration between Hovione Ltd, a pharmaceutical contract development and manufacturing company, and University College Cork to detect Hovione's APIs in wastewater. SPE-CE methods were developed for two of Hovione's APIs: 17NB26 (an antibiotic) and 05ZB23 (an anti-parasitic).

YO-21

Biosensing platform based on the combination of zeolite imidazolate framework and luciferase for rapid point-of-care of urinary tract infection

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Keywords: *Adenosine triphosphate determination, Bioluminescence, Enzyme, Sensor, Escherichia Coli*

The development of new methods for the rapid and efficient quantification of target analytes is one of the most challenging tasks for an analytical chemist. In this context, (bio)sensing can meet the demands of the new analytical chemistry. In this sense, special attention should be paid to the enzyme stability since it is such a key aspect in biosensor development, although other important features are also recommended such as fast response, user-friendliness and cost-effectiveness. Mutagenesis of cDNA encoding for target enzyme is one of the reported ways in order to achieve the above-mentioned desired characteristics. However, large expertise in this field is required as well as highly sophisticated logistics to work with. In this context, metal−organic frameworks (MOFs) have been shown merits to be a promising alternative as hosting platforms for their hybridization with proteins, especially enzymes, with the potential not only to keep protein integrity in harsh conditions, but also to improve their catalytic efficiencies [Chem. Rev. 121 (2021) 1077–1129]. In the present study, a new thermostable mutated luciferase [Biosensors 12 (2022) 742] has been attached to zeolitic imidazolate framework (ZIF-8) surface for the first time in order to improve both its stability and signal response. After the carefully optimization of this combination [Anal. Chem. 95 (2022) 2540–2547], the resulting bioluminescent (BL) composite (ZIF-8@luc) has shown improved characteristics. It is worth to highlight that the interesting findings were as follows: stability at low pH, in the presence of denaturing organic solvents and its storage at −20 °C. The biocomposite has been freeze-dried in a paper-based sensor and the quantification of adenosine triphosphate (ATP) from bacterial lysate has been carried out using portable silicon-photomultiplier detector. The all-in-one device outperformed the free luciferase sensor (x5-fold sensitivity) and it presented acceptable precision (RSD<20%) and limit of detection down to ~$4 \cdot 10^{-7}$ M. Surprisingly, the remaining BL activity at 25 ºC and 1 atm was not altered at least for 3 weeks and only 2 µL and 30 min are necessary to perform a real sample analysis. These results would help future works in the biosensing field to further develop alternatives for point-of-care diagnosis by using MOF-based materials.

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YO-22

Extraction of persistent organic pollutants from environmental water samples using a dynamic covalent polymer

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Keywords: *Dynamic covalent polymer, Persistent organic pollutants, Dispersive solid-phase microextraction, Gas chromatography, Mass spectrometry*

The use of polymers as sorbents has become essential in a wide number of analytical methodologies to develop adequate and efficient extraction procedures. However, these materials are usually discarded once used without considering their possible effects on the environment or even the possibility of their recycling, hence one of the current trends in this area is the development of sustainable materials with a high extraction capacity. Once used, a complete depolymerization of these polymeric sorbents into their constituent monomers would accelerate/facilitate their degradation, in addition to making it possible to make a circular use of them through the total or partial reuse of such monomers [Chemistry: A European Journal 24 (2018) 11255–11266]. Unfortunately, monomer recovery is often a complex and costly process, and recyclable polymers do not have the necessary thermal, mechanical, and chemical stability. A possible solution to this problem that has been overlooked to date is the use of “dynamic covalent polymers (DCPs)” as sorbents that have been shown to have a high capacity to be quickly and effectively recycled into their original monomers [Macromolecules 54 (2021) 10428–10434]. However, many DCPs described so far do not meet the desirable characteristics as extraction sorbents.
In this work, a DCP based on tetrazines has been applied for the first time to the extraction of 49 persistent organic pollutants (polycyclic aromatic hydrocarbons, organochlorine pesticides, polychlorinated biphenyls and antibacterial agents) from seawater and wastewater samples using gas chromatography coupled to mass spectrometry for their determination. This polymeric sorbent stands out not only for its high thermal stability and compatibility with aqueous media in a wide pH range, but also for its good extraction capacity, providing recovery values in the range 70-120%. Once used, the polymer can be completely recycled in its constituent monomers through the application of simple chemical stimuli (adding thiols such as cysteine in basic water), which makes it a good recyclable alternative for use in sample preparation.

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YO-23

Exploring the potentialities of a starch-based biodegradable polymer in white analytical chemistry: Study on the extraction of emerging contaminants from water samples

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Keywords: *White analytical chemistry, Biodegradable films, Film-based sorptive extraction, Emerging contaminants*

In recent years, there has been a growing interest in greener approaches in several fields, including analytical chemistry. Nevertheless, in the development of a new analytical method, some essential requirements, including time and cost-effectiveness, are not easily fulfilled through the greenest strategies. Therefore, Nowak et al., [TrAc–Trends Anal. Chem. 138 (2021) 116223] recently introduced the concept of "White analytical chemistry", which highlights the importance of being "greener" without neglecting the value of method performance and feasibility.
In this framework, it is fundamental to develop novel methods, which guarantee the achievement of accurate quantitation results with minimum use of toxic substances and waste production. Nowadays, one of the major analytical challenges is the detection of emerging contaminants (ECs) in environmental samples, due to their "pseudo-persistence" and trace concentration levels. Among them, a novel class called PMOCs (persistent mobile organic contaminants) deserves special attention, due to their hydrophilic characteristics. The extraction of these compounds from water samples by green and sustainable materials, followed by reliable analytical determination, is of utmost importance. Herein, we present a systematic study exploring the analytical applicability of a starch-based biodegradable polymeric film for the sorption of a plethora of 40 ECs that cover a wide polarity range, including pharmaceuticals, UV-filters, pesticides, hormones, tracers and perfluorinated compounds. The selected material, Mater-Bi (by Novamont), is a patented blend mainly constituted of starch and fatty acids, whose analytical potentialities have never been investigated, and that may be used for solid-phase extraction methods. In this work, Mater-Bi was tested in the form of flexible films, by studying the interaction with the considered analytes, for a possible application in a "film-based sorptive extraction". First, a recovery study was performed by simply spiking a small volume of a standard solution containing all analytes over the film and letting it dry. The film was rinsed with water to remove all substances with no or extremely weak interaction with the polymer surface and then an elution with MeOH was performed in an ultrasonic bath. Both the rinse and elution solutions were analysed by HPLC-MS/MS to determine the washed, eluted and retained fractions of each compound. The results indicated a rather heterogeneous behavior, depending on the chemico-physical properties of the compounds. A clear distinction was observed between three groups: (i) very polar analytes (logD<0), which were almost completely removed by the washing step; (ii) mid-polar analytes with acidic properties, whose recovery in the eluate was approximately 50% and (iii) rather hydrophobic analytes (logD>4), such as UV-filters, which were quantitatively recovered in the eluate. Along with the recovery, the matrix effect in the extracts was estimated and resulted moderate or negligible for most compounds, indicating that no interference was given by the polymer during the treatment steps. Based on the affinity with an analyte, this material may be applied either for exhaustive or equilibrium extraction methods. To explore these possibilities, a series of experiments involving the immersion of Mater-Bi pieces into a small volume of spiked water, for a fixed time, was performed. Given the variety in the analytes' properties, the multivariate approach of experimental design was employed to simultaneously investigate several factors, possibly affecting the interaction mechanism. The factors, varied within a selected experimental domain, were pH, NaCl concentration, temperature, film dimension and % of organic modifier (EtOH), while the chromatographic signals in the eluate were used as responses to be modeled. A principal component analysis highlighted the correlation among some of the responses, indicating a similar behavior for some groups of substances. Multiple linear regression was employed to model the responses as a function of the independent variables, providing information about the effect of these variables on the material-analyte interaction. The addition of NaCl resulted particularly favorable for the interaction of perfluorinated compounds. For all non-steroidal anti-inflammatory drugs and the antibiotic tetracycline, a significant dependence on pH, temperature and film dimension was observed. Estrogens sorption was affected by the film dimension and the organic modifier presence. Besides, two further extreme situations were observed: a group of rather polar analytes, including several pharmaceuticals, slightly accumulated onto the film, independently from the experimental settings; on the other hand, UV filters and the anti-bacterial triclosan were exhaustively extracted from water in all experiments, with low variability. These outcomes suggest that this biodegradable material may be an interesting choice in different analytical applications involving a wide range of analytes, optimizing the material configuration and pre-treatment strategy, depending on the target species.

YO-24

Recycled polylactic acid-based nanocomposites for water remediation and sample pretreatment

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Keywords: *Polylactic acid, Nanocomposite, Water remediation, Sample preparation, Contaminants*

The increasing presence of a wide variety of contaminants in the environment calls for the development of new strategies aimed at removing and minimizing their adverse impact on natural ecosystems. In particular, the environmental sector that requires a prompt action is the hydrosphere. As global population continues increasing, the pressure on water supplies is inevitably intensifying and the development of new technologies is an urgent need.
In this study, the main objective was the realization of a sorbent nanocomposite, prepared through the recycling of polylactic acid (PLA) from waste materials such as PLA sheets recovered from a tobacco product for the non-burning technology. A washing procedure was optimized to obtain regenerated raw material. Among the wide group of solvents tested for the PLA regeneration, tetrahydrofuran (THF) was chosen as the dissolving agent. With the technique of the emulsion precipitation, the organic phase saturated with PLA was combined with a water solution, saturated with sodium chloride. As a result of the salting-out effect, the organic and aqueous phases were immiscible, and a cloudy solution was formed under magnetic stirring. The addition, drop by drop, of water to the emulsion broke the emulsion and promoted the precipitation of PLA in the form of nanospheres. With the aim of obtaining nanocomposite sorbents, some carbon-based coadjutants were selected: active carbon (PLA@AC) for water remediation purposes, while carbon nanotubes (PLA@CNTs) for solid-phase extraction (SPE) applications. The secondary component of the composite was added to the organic PLA solution in THF. An entire characterization study was performed via SEM and TEM analysis, as well as FTIR for the qualitative confirmation of the obtained material composition. The PLA@AC nanocomposite was used as sorbent for the removal of contaminants from water. The contaminants from different chemical classes allowed one to verify the applicability and effectiveness of the procedure. For all the selected analytes, the removal capability of the PLA@AC was higher than 80% of the total. The reproducibility, in terms of RSD% inter batches of the same material was less than 10%. Regarding the PLA@CNTs nanocomposite developed for the SPE applications, very good recoveries were achieved with aromatic analytes as well as with non-polar analytes. Such device can be used both packed in a cartridge and dispersed in an aqueous sample to perform dispersive-SPE.
The presented material has favorable characteristics for the environmental remediation and for applications on a lab scale. Ideal peculiarities of such composites are the sustainability (recyclability of the PLA and its complete biodegradability) and the simplicity of their realization. The perfect compatibility of PLA with different secondary components enables to control the adsorption capabilities of the material depending on specific requirements.

YO-25

Biorefinery approach for the revalorization of leaves from *Citrus reticulata* to obtain antioxidant and anticholinergic extracts

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Keywords: *Supercritical fluid extraction, Natural deep eutectic solvents, Terpenoids, Phenolic compounds, Sustainable extraction*

Tangerine (*Citrus reticulata* L.) is a fruit well-known for its antioxidant, anti-inflammatory, cardioprotective and anticarcinogenic properties. Tangerine leaves are one of the main post-harvest wastes that contain terpenoids and phenolic compounds with interesting beneficial properties for the health, and that are usually discarded. Mainly, the extraction of these bioactive compounds from plant matrices has been carried out by conventional extraction techniques with poor selectivity, spending high volume of organic solvents and providing low extraction yields. To replace conventional extraction techniques, supercritical fluid extraction (SFE) and natural deep eutectic solvents (NADESs) have been considered in this study as more sustainable and selective extraction techniques for the recovery of bioactive compounds. In this sense, the aim of this work was to develop a biorefinery process by a sequential extraction of terpenoids and phenolic compounds with antioxidant and anticholinergic capacities.
First, an optimization of SFE method to obtain bioactive terpenoids was carried out using different extraction temperatures and pressures. A temperature of 60 °C and 200 bar of pressure provided the extracts with the highest antioxidant capacity measured by ABTS and DPPH assays and, anticholinergic capacity measured by AChE and BuChE assays. Besides, gas chromatography-mass spectrometry (GC-MS) analysis reflected the highest terpenoid content in the extracts obtained under these extraction conditions. Then, a green extraction methodology was developed for the recovery of bioactive phenolic compounds from the residue of the optimized SFE using ultrasound-assisted extraction (UAE) combined with NADES. Twelve NADESs were studied to select the best one to recover phenolic compounds from tangerine leaves. Choline chloride:glycerol with a molar ratio of 1:2 was the NADES selected as the best extraction solvent to release antioxidant and anticholinergic phenolic compounds from tangerine leaves. A Box-Behnken experimental design was used to optimize UAE extraction conditions such as water content (10-60%, v/v), temperature (25-100 °C) and extraction time (15-150 min). Results showed that 43% water in NADES, a temperature of 25 °C and an extraction time of 50 min provided extracts with the highest total phenolic content (measured by Folin-Ciocalteu assay), antioxidant capacity (in ABTS and ORAC assays) and anticholinergic capacity (AChE and BuChE assays). In addition, the optimum extract was compared with extracts obtained at the same extraction conditions but using 100% water and 100% NADES as extraction solvents. This comparison among extracts showed that a decrease or an increase in water percentage has a negative effect in the extraction of bioactive phenolic compounds with regard to optimum extract.

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YO-26

Sample preparation metric of sustainability. A new tool to assess analytical sample preparation procedures

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Keywords: *Sample preparation, Analytical extractions, Green analytical chemistry, Greenness metrics*

Sample preparation is a key step in most analytical methods, generally regarded as the least green step of the entire procedure. Current existing green metrics such as Green Analytical Procedure Index (GAPI), Complementary GAPI (complexGAPI), Analytical GREEnness Metric (AGREE), and Analytical greenness metric for sample preparation (AGREEprep) assess the greenness of sample preparation techniques through the evaluation of the whole analytical procedure: including sampling steps, transportation, sample preparation, and the final detection/quantitation. Such inclusion of the entire method makes assessing the sustainability of a newly developed sample preparation technique challenging, as many aspects not directly related to the sample preparation step by itself are considered in the resulting assessment. As result, the results when analyzing the greenness of novel sample preparation methods can be distorted by those other factors that are not relevant in terms of sample preparation procedure. Besides, current existing metrics do not allow to make fair and clear comparisons between similar sample treatment procedures. Thus, an alternative metric that can explicitly and exclusively evaluate the sample preparation is needed. In this work, we propose a new metric focused on the assessment of the sample preparation step. The metric is simple and user-friendly; it reports the result with a clock-like diagram, displaying the greenness outcome of main sample preparation parameters and a total score. Besides, this new metric can be used for differentiating closely related microextraction approaches in terms of sustainability.

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YO-27

How to analyze fatty acids and fatty acid methyl esters in water samples simultaneously

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Keywords: *Solid-phase microextraction arrow, Fatty acids, Fatty acid methyl esters, Derivatization, Gas chromatography-tandem mass spectrometry*

Fatty acids (FAs) and fatty acid methyl esters (FAMEs) are important substance classes for example in the food industry, medicine, microbiology, water analysis, and biodiesel production. FAs mostly occur in higher concentrations than FAMEs and are in general more intensively studied. However, FAs and FAMEs are related and often appear together, as they can easily be transferred into each other. Due to this, the simultaneous determination is of advantage, but until now, no established method exists. One reason for this may be that generally methyl esterification is utilized as a derivatization technique for FAs in GC analysis, which makes it impossible to distinguish the FAs and FAMEs.
The full method was automated using a RTC PAL autosampler with various modules and combines in-situ derivatization with solid-phase microextraction arrow. Esterification parameters (pH, time, temperature, CD_3OD content) were optimized by design of experiment and the solid-phase microextraction arrow has been optimized in our previous study. For the analysis of FAs and FAMEs, a GC-MS/MS method operating in MRM mode was developed. The method was tested and validated in different real water samples such as from a lake, wastewater treatment plant, and bioreactor.
The FAs were transformed to d3-FAMEs during in-situ derivatization reaction in water and could be selectively distinguished from FAMEs by the chromatographic isotope effect resulting in a retention time shift of ΔRt = 0.03 min and the mass shift of +3 m/z. The optimal derivatization conditions were found to be 20 min, 50 °C, 4 v/v% CD_3OD, and pH 2.1. Method validation showed good linearities and method detection limits of FAs and FAMEs in different matrices. FAs and FAMEs were detected and quantified in real water samples of different origins, showing that a simultaneous method could be useful for various applications.

YO-28

Miniaturized stir bar sorptive dispersive microextraction as a high-throughput and feasible approach for low-availability samples

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Keywords: *Bioanalysis, Biomarkers, Magnetic sorbent, Miniaturization, Stir bar sorptive dispersive microextraction*

Large volumes of biological samples are often not available either because of the nature of the sample itself (*e.g.*, saliva, semen, follicular fluid, cerebrospinal fluid) or because of the characteristics of the person under study (*e.g.*, newborns, immunosuppressed or anemic patients). Besides, target compounds are usually at trace level and biological fluids are really complex matrices. Therefore, the development of sample treatment procedures (to extract and preconcentrate analytes) that minimize the amount of sample needed for the analysis is interesting and of paramount importance in the context of bioanalysis.

In order to contribute to the development of new feasible and high-throughput approaches that allow the sample treatment of low-availability samples, the miniaturization of stir bar sorptive dispersive microextraction (mSBSDME) is presented in this communication [Anal. Chim. Acta 1238 (2023) 340627]. This new methodology is based on the principles of stir bar sorptive dispersive microextraction, but the amount of sorbent and, most importantly, the amount of sample are considerably reduced to a tiny amount and a few microliters, respectively.

Thus, affordable 400-µL flat-base glass inserts and minute bar-shape neodymium magnets (3 mm length x 2 mm diameter) were used as extraction devices hold by a specifically designed multiextraction assembly, which comprises a high-rate stirring plate and a 3D-printed support to treat 15 samples simultaneously. This new approach allows a fast, affordable, portable, and high-throughput analysis of low-volume samples, expanding the potential of the technique. The same extraction device is used along the different stages, thus avoiding transfers, which reduces sample handling. Besides, the reduction in the sample, sorbent and organic solvent amounts allows a considerable decrease of the waste generation, and thus pursues a green sample preparation for bioanalysis.

As a proof-of-concept of this new methodology, cortisone and cortisol were determined in human saliva using a composite material made of a reversed phase polymer (Strata™-X-RP) and $CoFe_2O_4$ magnetic nanoparticles. Liquid chromatography coupled to tandem mass spectrometry was used to measure both analytes obtaining good analytical features in terms of linearity ($R^2 > 0.997$), method limits of detection and quantification (22.6 and 75.5 $ng \cdot L^{-1}$ for cortisone, and 19.3 and 64.3 $ng \cdot L^{-1}$ for cortisol, respectively), repeatability (RSD ≤ 11%) and relative recoveries (78–134%).

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YO-29

High-throughput and automated solid-phase microextraction-liquid chromatography-mass spectrometry system for the analysis of mycotoxins in beers

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Keywords: *Solid-phase microextraction, High-throughput, Automation, Mycotoxins, Beer*

Determination of compounds that affect human health and well-being is of special interest. Mycotoxins are relatively wide spread contamination in many food products. Since they are formed as secondary metabolites of certain molds, which might infect the majority of food products. Appropriately packed food is protected from their formation, however very often the intermediate products in the production chain might be infected since their storage is frequently not adequate. One example of a food product that might be a potential source of mycotoxins is beer. These toxic compounds can originate by barely infection by fungi; therefore, mycotoxins might transfer from it to the finished product. Since most mycotoxins are stable substances, which tend to survive storage, processing, or even high temperatures, therefore they might occur in beer after all technological processes. The monitoring of each step of technological production is very important. Herein we focus on the development of a SPME blade-LC-MS/MS technique dedicated to the analysis of mycotoxins in beer samples. Additionally, the fully automated 96-concept was used during the stage of sample preparation to demonstrate the possibility of automation to reduce human labour and increase reproducibility.
It was demonstrated that the commercial SPME blade with matrix-compatible hydrophilic-lipophilic balance (HLB)/polyacrylonitrile (PAN) coating showed good results in terms of extraction efficiency, as well as their reusability. The PAN binder forms a thin-film, which functions as barrier that allows the extraction of small molecules while insulating the sorbent particles from contact with large molecules such as protein and cell matter, then quickly washing step by water can remove the salts and non-specific attachments on the coating surface. Carry-over from the samples was easily removed by using the additional step of sample washing, which allowed to use of the coated blades multiple times. The possibility of the method used in the quantitative analysis was also evaluated and it demonstrated satisfying linearity – R^2 was > 99% for all analytes. The observed linearity in the range of 1-200 ng/mL or even wider for some of them will definitely allow for reliable quantification in beer samples. The matrix effect, which is an important factor in food analysis, was evaluated and it was around 5% for all 8 mycotoxins. Also, addition of internal standards was further decrease in matrix effect. The sensitivity of the proposed technique was investigated, and the limit of detection (LOD) and limit of quantitation (LOQ) were between 0.02-3.0 ng/mL and 0.05-10 ng/mL respectively. These values were comparable with alternative laborious extraction methods. The achieved results allowed us to conclude that SPME blades-LC-MS/MS is a reliable quantitation method for the analysis of mycotoxins in beer samples. It allows determination of mycotoxins presence below levels regulated by safety agencies. Moreover, the possibility of further coupling the technology with direct mass spectrometry analysis will create the possibility of an efficient low cost, high throughput and performance green method.

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POSTER COMMUNICATIONS

P-01

Enhanced extraction protocols for recent emerging organic contaminants adsorbed onto microplastics

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Keywords: *Microplastics, Emerging organic contaminants, Ultrasound-assisted extraction, Liquid chromatography, Mass spectrometry*

Microplastics have long been considered major pollutants of the seas and oceans. Their ability to adsorb other organic matter and thus act as a vector of contamination has also long been investigated. There are several studies confirming this. In our study, we have focused on the most recent organic compounds considered to be the latest emerging environmental contaminants according to EU.
One of the extraction techniques for organics adsorbed on microplastics is the ultrasound-assisted extraction. This is a simple and effective method suitable for the problem at hand. In order to examine the impact of various factors on the extraction of analytes from MPs using ultrasound-assisted extraction, we employed an experimental design with Minitab® software. This approach allowed us to assess the individual influence of each variable on the extraction process as well as to investigate potential correlations among the variables. The experimental design was performed in two steps. At first, we have studied the extraction with three variables (solvent type, extraction time, solvent volume) at two levels and the fine tuning of the extraction was done with two variables at three levels (solvent type, extraction time). After extraction, an ultra-high performance liquid chromatography system coupled to a triple quadrupole mass spectrometer (UHPLC-MS/MS) was employed to separate and detect analytes. The responses varied based on the specific chemical properties of the contaminants as expected and for most of the compounds, relative extraction recoveries were in the range from 80-120%.
Furthermore, the enhanced methodology will be implemented to analyze samples of microplastic fragments and plastic pellets collected from diverse tourist and secluded beaches across the Canary Islands archipelago (Spain). This assessment aims to determine the occurrence of these emerging contaminants within the microplastic residues.

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P-02

Microwave-assisted extraction of antidepressants from fish tissue

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Keywords: *Antidepressant compounds, Fish tissue, Microwave-assisted extraction, Liquid chromatography, Mass spectrometry*

The presence of antidepressants in aquatic environments can have adverse effects, even at low concentrations. While most research has focused on detecting these compounds in wastewater, few studies have examined the impact on aquatic organisms that are exposed to these polluted waters. Wastewater treatment plants do not effectively degrade these compounds, making it important to investigate their effects on aquatic life.
This study presents an optimized analytical method for extracting and quantifying four commonly used antidepressants (venlafaxine, citalopram, sertraline, and fluoxetine) and two of their metabolites (o-desmethylvenlafaxine and norsetraline) from fish tissues using microwave-assisted extraction and ultra-high performance liquid chromatography coupled with tandem mass spectrometry.
Under optimal conditions, the method yielded recoveries ranging from 70-120%, with deviations lower than 20% in most cases, depending on the species and concentration tested. No strong matrix effect was observed, so there was no need to apply a clean-up step. Quantification of real samples was performed by matrix-matched calibration, with method quantification limits ranging from 2.59-196 ng/g depending on the compound.
The developed analytical method was successfully applied to extract and determine the target compounds from fish caught in aquaculture traps in seawater off the coast of the Canary Islands. Three main antidepressants were detected, but only two could be quantified: citalopram (5.83 ng/g) and sertraline (6.58 ng/g). This study highlights the importance of monitoring and reducing the presence of antidepressants in aquatic environments to mitigate their potential adverse effects on aquatic life.

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P-03

PFAS screening and quantitation with SPME and direct ionization with DART mass spectrometry

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Keywords: *Polyfluoroalkyl substances, Chromatography free, Solid-phase microextraction, Direct analysis in real-time, Mass spectrometry*

The chromatography free techniques are emerging solutions which offers rapid, easy and direct analysis. A very attractive for many analytical problems. In this case we use the DART technology coupled to mass spectrometry to help resolving an environmental well-known problem for screening and quantitation of PFAS. Nevertheless, the promising of these technologies, several challenges in sample preparation are to be addressed. In this work, we present the coupling with SPME for sample preparation and clean up improving the selectivity and detection limits of the analytical methodology. Further developments of these technologies may allow in a short future to work in a routine basis with chromatography free techniques for environmental monitoring and other rapid “in-situ” control strategies.

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P-04

Determination of tetracyclines in wastewater using an automated method for the solid-phase extraction followed by fluorimetric detection

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Keywords: *Automation, Tetracyclines, Solid-phase extraction, Fluorimetric detection, Wastewater analysis*

Tetracyclines are used as antibiotics in human, veterinary, agricultural and livestock medicine. The widespread application of these pharmaceuticals leads to an accumulation of their residues in the environment. This contributes to bacterial resistance and harms human and environmental health. They are the most common antibiotics found in wastewater and can cause inhibition of the biological treatment of wastewater in treatment plants. For this reason, a fast, sensitive and precise method is needed for its detection in wastewater treatment plants.
This work presents a multisyringe flow injection analysis (MSFIA) system for the automatic extraction and determination of tetracyclines in wastewater samples.
The sample was adjusted with McIlvaine-Na_2EDTA buffer before solid-phase extraction with an Oasis HLB column, used for the analyte preconcentration. The europium (Eu^{+3})-based and citrate-mediated method (using Tris-HCl buffer) was selected for the fluorimetric analysis (λ_{exc}= 400 nm, λ_{em}= 612 nm). For fluorescence detection, a low-cost system consisting of an USB 2000 CCD detector and a 3D-printed support that stores an LED light source was used. The extraction and detection parameters, including sample volume, elution solvent, elution volume and flow rate, solvent concentration, europium/citrate concentration and pH, were systematically optimized.
The proposed method provided low limits of detection (9.4 $\mu g \cdot L^{-1}$) and quantification (31 $\mu g \cdot L^{-1}$), and good values for intra-day (< 4%) and inter-day precisions (< 6%). An enrichment factor of 40 was obtained. Recoveries of spiked tetracycline in wastewater samples (inlet, outlet and secondary settler) ranged from 87 to 106%. Finally, the results of this work were compared with those obtained by the reference method commonly used for tetracyclines detection, namely liquid chromatography coupled to a fluorescence detector (UPLC-FLD).
To the best of our knowledge, this study presents the first automation of tetracycline determination using the europium-based method and incorporating preconcentration and extraction steps. This method offers several advantages, including high sensitivity and reduced analyst intervention. Additionally, the proposed system avoids the use of expensive instruments (e.g. chromatographs) and helps mitigate potential environmental damage resulting from the disposal of mobile phase solvents commonly used in liquid chromatography.

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P-05

Determination of microplastics in Cuvierian tubules and digestive tracts of the sea cucumber *Holothuria sanctori* from Tenerife (Canary Islands, Spain)

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Keywords: *Microplastics, Sea cucumber, Digestion, Canary Islands, MicroFourier transform infrared spectroscopy*

Holothuria sanctori is an echinoderm that lives in the rocky sea holes of the Canary Islands [Anales de Biología 3 (1985) 13–36]. It is a deposit-feeder organism with an important role in bioturbation as it consumes and excretes huge amounts of sediments per year. Thus, sea cucumbers may merge and move sediments containing microplastics, as it has been widely reported in the literature [Mar. Pollut. Bull. 135 (2018) 376–385]. Besides, *H. sanctori* also has the ability to discharge the Cuvierian tubules as a defense system when they are at risk, which are connected with the respiratory tree. Therefore, since respiratory trees may be a potential channel for the entrance of microplastics in the Cuvierian tubules and that sea cucumbers can daily intake huge amounts of sediment without covering long distances, the object of this study is to determine the presence of microplastics in *H. sanctori* 's digestive tract and Cuvierian tubules.
For that purpose, 21 sea cucumbers were sampled in intertidal pools at Punta del Hidalgo (Tenerife, Canary Islands, Spain) by snorkeling. Samples were frozen at -20 ºC until further analysis. The longitudinal dissection for the extraction of the digestive tract and Cuvierian tubules was carried out after biometric measurements (total length and color). Then, they were weighted and digested with 33% w/v H_2O_2 at 50 ºC for 48 h. Afterwards, due to the high amount of sediments in the digestive tract after the digestion, a density separation by flotation with a NaCl saturated solution was carried out. Finally, samples were filtered through 50 µm pore size stainless-steel filters. The flotation procedure was repeated four times for each digestive tract sample. Concerning the Cuvierian tubules, they were also directly filtered through 50 µm pore size stainless-steel filters. Finally, all the filters were visualized under a binocular stereoscopic microscope and the microplastics found were characterized by shape, size and color. Their composition was determined by microFourier transform infrared spectroscopy.

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P-06

Optimization of an analytical method based on micro-matrix solid-phase dispersion combined with gas chromatography-mass spectrometry for the determination of nine bisphenols in mussel samples

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Keywords: *Bisphenols, Micro-matrix solid-phase dispersion, Gas chromatography-mass spectrometry, Mussels*

Nowadays, bisphenols (BPs) are widely used in industry for the manufacture of resins and plastics. They can be present in paints, printing inks, mechanism device, thermal paper, personal care products, baby bottles and in all utensils intended to come into direct contact with food. European Chemicals Agency (ECHA) considers BPA as one of the endocrine disruptors. In environmental samples, BPA and its analogues were found in wastewater, rivers, ground water, surface water, marine water and sediment, and biota samples in high concentrations [Mar. Pollut. Bull. 106 (2016) 360–365].

The aim of this work is the optimization and developing of a new, rapid, sensitive, cheap and reproducible procedure based on miniaturized MSPD (micro-MSPD) in glass Pasteur pipette coupled to GC-MS for determination of nine BPs (BPAF, BPF, BPE, BPA, BPG, BPC2, BPZ, BPS and BPM) in mussel samples. To increase volatility and thermal stability and reduce polarity of analytes, derivatization with 99% N,O-bis-(trimethylsilyl)trifluoroacetamide + 1% trimethylchlorosilane (BSTFA+1%TMCS) was necessary. In order to improve the clean-up step, EMR-Lipid technology was applied in order to remove lipids from mussel extracts.

The sample preparation was optimised by studying the following parameters: C_{18} clean-up agent amount (C_{18} as a co-column packed), C_{18} extractant/dispersant agent amount and elution volume (methanol). In relation to the further clean-up step, EMR-Lipid amount and methanol/water (80/20) volume parameters were optimized. EMR-Lipid sorbent was chosen because it selectively removed lipids in many extraction processes. Several experimental proofs were carried out studying each variable separately.

According to all the experiments, the optimized micro-MSPD method consisted of 50 mg of freeze-dried mussel, 50 mg of Na_2SO_4 anhydrous, 300 mg of C_{18} (extractant/dispersant agent), 100 mg of C_{18} (clean-up agent as a co-column packed) and 2 mL of MeOH, and the second clean-up step consisted of 150 mg of EMR-Lipid and 600 µL of mixture MeOH/H_2O (80/20). The optimal experimental conditions of derivatization procedure were 200 µL of BSTFA+1% TMCS at 60 ºC for 60 min.

The optimized method was validated in terms of sensitivity (LOQ), accuracy (recovery) and precision (RSD). The limits of quantification (LOQs) of the whole method were calculated as the concentration giving a signal to noise of ten (S/N=10) and ranged from 0.014 to 4 µg/kg dry weight. The recovery studies were performed by applying the optimized method to a sample spiked at two levels of concentration, 50 µg/kg dry weight (low level) and 100 µg/kg dry weight (high level). Good recoveries were obtained, from 51.2 to 93.8% at low level and from 65.7 to 109% at high level. The relative standard deviations (RSDs) varied from 0.6 to 13%.

The method was validated and applied to four real mussel samples (two raft mussels and two wild mussels) from Galician Rías, Barqueiro, Ares-Betanzos, Arousa and Vigo. All compounds were quantified in the studied samples, except BPAF in the raft mussel coming from Ría de Arousa.

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P-07

Optimization of micro-QuEChERS extraction coupled to gas chromatography-mass spectrometry for a fast determination of phthalates in mussel samples

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Keywords: *Phtalates, QuEChERS, Gas chromatography, Mass spectrometry, Mussels*

Phthalic acid esters (PAEs) are the most commonly used plasticizers in the world. They are intended for a wide variety of applications, as construction, food packing, electronic devices, personal care products, etc. Since they do not bond to plastic polymer covalently, levels of phthalates are extensively found in all environmental compartments such as sediment, water and biota [Environ. Int. 26 (2019) 635–643]. Shellfish as mollusc bivalves accumulate contaminants from the marine environment making them a risk to human and food web. Mussels have been used for international monitoring as excellent bioindicators of the pollution of coastal and estuarine waters.

In this work a new miniaturized version of the analytical method based on the Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) technique using Florisil in the cleanup step for extracting six PAEs, dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), benzyl butyl phthalate (BzBP), diethyl hexyl phthalate (DEHP) and di-n-octyl phthalate (DnOP), in mussel samples was developed by using an experimental design. A full orthogonal factorial (2^4) type V+ resolution design with a central point has been selected involving 17 randomized runs. Four factors were studied, ultrapure water/ACN volumes (Factor A), extract pouches amount (Factor B), Florisil amount (Factor C) and sample amount (Factor D). The sample preparation method was followed by GC-MS (SIM).

The optimized micro-QuEChERS method, according to factorial design and further experiments, consisted of 0.1 g of freeze-dried mussel, 0.5 mL of ultrapure water, 0.5 mL of ACN, 0.3 g of Agilent Technology extraction salt packet and 0.05 g of Florisil. The whole method was validated at two concentration levels. Recoveries ranged from 78.7 to 107.5%. Reproducibility in terms of coefficients of variation was between 4.9 and 12.1%. Quantification limits of the method were between 0.53 and 38.0 µg/kg dry weight. Five mussel samples coming from the Galician Rías were analysed using this method. Except for three of five samples where DnOP was below the limit of quantification, all PAEs were found in concentrations that ranged between 1.99 and 372.7 µg/kg dry weight.

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P-08

Sample preparation analysis methods of microplastics

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Keywords: *Textiles, Microplastics, Sample preparation*

This research study was carried out in collaboration between Aquafil Spa and CNR STIIMA (Biella Department) with the aim to establish a standard method applicable to the determination of microplastics (MPs) in different textile matrices such as water samples from the textile production process and/or from the washing of clothing (e.g. garments or other textiles). European Chemicals Agency (ECHA) for EU Commission defines “microplastic” as material consisting of a solid polymer containing particles, to which additives or other substances may have been added, and where ≥ 1% w/w particles have all dimensions 100 nm ≤ x ≤ 5 mm, or, for fibres, a length of 300 nm ≤ x ≤ 15 mm and a length/diameter ratio > 3 [ECHA, European Chemical Agency - ANNEX XV Restriction Report].
In the case of those released by textiles, the typical morphology it is the fibrous one and their diameter and length can vary depending on the construction parameters of yarns and fabrics during processes or on washing conditions (temperature, detergent, time).
Depending on the textile matrix, it may be necessary to pre-treat the sample to concentrate the microplastics and eliminate inorganic (salt) and organic contaminants (e.g. biological, dyes) that could interfere with their identification. The method involves a preliminary observation of the sample under an optical microscope, filtration and subsequently identification, counting of microplastics collected through the filter by vibrational spectroscopy such as Micro-FTIR (Fourier Transform InfraRed Spectroscopy coupled with optical microscopy) and Micro-Raman (Raman Spectroscopy coupled with optical microscopy).
In the case of samples of unknown origin, a series of pre-screening tests are provided for the possible presence of salts or organic matter. For aqueous samples, standard tests such as conductivity [Agency for environmental protection and technical services, APAT 2030, manual 29 (2003)], chemical oxygen demand (COD) [Agency for environmental protection and technical services, APAT 5135, manual 117 (2014)], total suspended solids (TSS) [Agency for environmental protection and technical services, APAT 2090B, manual 29 (2003)], and optical microscopy (OM) for fibres identification and evaluation of image quality are recommended.
Pre-treatments can be necessary before filtration of the washing effluent with a 15% H_2O_2 solution for a duration between 7-30 days to eliminate any trace of organic matter without damage MP including different pre-treatments. Salt removal can be carried out by dosing a solution of 0.1 mol/L of acetic acid (with a volume fraction of 60%). The molarity of the solution can be increased to make the removal of salt or organic material more efficient. Always depending on the pre-screening in OM it will be possible to decide to perform a pre-dilution with water from the starting sample in order to produce a sub-sample to be tested.
The work is in progress (ISO/FDIS 4484-2) and it is part of a method presented to ISO (International Organization for Standardization) for the evaluation of microplastics in the textile sector, which could prove suitable for the analysis of microplastics of different origins.

P-09

Pipette tip solid-phase microextraction packed with graphene nanoplatelets and smartphone-based fluorescence detection to determination of sulfonamides in environmental waters

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Keywords: *Total sulfonamides, Pipette tip solid-phase extraction, Graphene nanoplatelets, 3D detection platform*

Recent significant advances in the miniaturization of spectroscopic analytical instruments have enabled the development of screening methods of contaminants of emerging concern (CECs) in water samples, which are rapid, low-cost, portable, easy-to-use analytical techniques before using more powerful and expensive reference analytical methods. A sensitive, miniaturized, and low-cost method combining pipette tip solid-phase microextraction and smartphone-based fluorescent detection has been developed for determination of total sulfonamides in water samples. Sulfonamides antibiotics (SAs) are contaminants commonly found in water matrices, leading to antibiotic-resistant bacteria and risks to human health and the environment. Among SAs detected, sulfamethoxazole (SMX) is the most common found in environmental samples analyzed and has also been included in the 3rd Watch List of substances recommended for monitoring in the European Union in the Framework Directive of the water. For this reason, its real-time monitoring is essential in WWTP effluents for subsequent risk assessment. Sample preparation consisted of preconcentration of SAs using graphene nanoplatelets packed inside a pipette tip, followed by fluorescent derivatization using fluorescamine inside the microplate reader, both 3D-printed. Subsequently, a 3D-printed detection platform that houses monochromatic LED strips as radiation source and a smartphone as detector have been used for determination total SAs. Digital image processing was based on the RGB color model using ImageJ software with its readplate plugin and the green intensity channel was used as analytical signal due to its higher sensitivity. Several factors that affect the extraction efficiency and the detection system used have been optimized. Under the optimized conditions, good linearity for SAs studied (SMX, SDX, SMR and SMZ) were obtained in a range of 10-60 $\mu g \cdot L^{-1}$ with correlation coefficients ≥0.990 and limits of detection between 2.5-3.1 $\mu g \cdot L^{-1}$ for a sample volume of 10 mL. The recoveries of SMX (as a model compound to express total SAs) spiked in the samples tested at two different levels showed good recoveries from 94 to 102% with RSD ≤7.6% and the results obtained with proposed system, were compared with a conventional spectrofluorometer (P ≥0.13).

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P-10

3D-printed device coated with Zn/Co-ZIF for the on-site extraction of fluoroquinolones from water samples prior to HPLC-FL analysis

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Keywords: *3D-printed device, On-site extraction, Bimetallic porous carbon, Fluoroquinolones, Online flow system*

Fluoroquinolones (FQs) have been widely used to treat various diseases in humans and animals. These components and their metabolites are frequently found in environmental waters since they are poorly absorbed by the organism, and as a result, around 70% of them are excreted into the environment, which with their low biodegradability; promote the development of antibiotic resistance genes (ARGs). Unfortunately, wastewater treatment plants (WWTPs) do not completely remove these pseudo-persistent and recalcitrant compounds, thus their continued entry into the aquatic environment, even in low concentrations, can cause potential risks to terrestrial and aquatic ecosystems, representing a great threat to human health. Thus, their monitoring is essential, however, due to their low concentrations, a simple and efficient pretreatment process is necessary to extract and preconcentrate prior to instrumental analysis. A 3D-printed device covered with Zn/Co-ZIF bimetallic porous carbon material was developed for the in-situ extraction of FQs in wastewater samples and subsequent elution and determination in the laboratory using an online flow system coupled to HPLC-FL. Different characterization techniques of the synthesized material were performed including scanning electron microscopy (SEM), X-ray diffraction (XDR), N_2 adsorption-desorption measurements and zeta potential. Likewise, several parameters that affect the extraction efficiency and desorption were optimized including the extractant immobilization technique on the 3D-device, extraction time, pH effect, sample volume as well as the type of eluent, eluent volume, and flow rate and recyclability. The main objective of this study is to improve the applicability of MOFs as adsorbents for in-situ extraction using small eluent volumes for desorption of target analytes and subsequent instrumental analysis.

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P-11

POPs extraction from marine microplastics - Factors that reduce extraction efficiency

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Keywords: *Microplastics, Persistant organic pollutants, Extraction efficiency, Gas chromatography, Degradation*

Every year, between 8 and 12 million tons of plastic are dumped into the ocean, primarily macroplastics (sizes larger than 2.5 cm). Over time, these plastics break down into microplastics (fragments ranging from 1 µm to 5 mm) [Sci. Total Environ. 788 (2021) 147802]. The composition of these plastics is highly diverse, as there are many types of plastics, and each can contain a different mixture of additives, providing them with different physicochemical properties. However, the most widely used plastics worldwide, and consequently the most abundant on the ocean's surface, are polyethylene and polypropylene.

In the ocean, persistent organic pollutants (POPs) are adsorbed onto marine microplastics (MPs) due to their chemical affinity (both are lipophilic compounds). The variety of POPs that adhere to microplastics is wide, but they can be classified into pesticides (organochlorine and organophosphate pesticides), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and dioxins, between others. This list also includes emerging contaminants, which tend to have higher polarity (they are more hydrophilic).

POPs extraction from marine microplastics is highly complex due to the extremely high affinity between the non polar pollutants and compounds of the plastic material, which hinders the process and can result in underestimated concentration values. The factors that affect the adsorption-desorption process of POPs onto microplastics, and therefore can influence the recovery percentages obtained in the extraction process prior to analysis, are as follows:

1. Time of residence in the ocean.
2. MPs degradation state, surface weathering, yellowing (higher with a longer residence time).
3. Relation surface/volume of microplastic surface (higher if the degradation state is high and for small fragments).
4. Microplastic composition: The polymer composition and additives present affect the adsorption-desorption process and, therefore, the extraction of POPs from microplastics.

In this study, a semi-quantitative methodology has been developed to perform a comparative assessment of POPs concentration in marine microplastics in the simplest way possible for such a complex matrix, using a routine analytical equipment, a GC-MS. This developed methodology is based on micro-solid-liquid-liquid extraction technique (µSLL extraction) with methanol and n-hexane as extractants [Water Air Soil Pollut. 232 (2021) 1–11]. Furthermore, a laboratory study has been conducted to evaluate the different factors that affect the recovery percentage, such as plastic composition, degradation state, surface weathering, and yellowing [Polymers 14 (2022) 1305].

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P-12

Microplastics identification in chocolate using micro-spectroscopy techniques

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Keywords: *Chocolate bars, Microplastics, Food, Spectroscopic technique, Silicon filter*

Plastics have become a global concern in both scientific and social circles, as they are utilized in a wide range of applications such as construction, packaging, household goods, sports equipment, gardening, and more. In daily life, examples of plastic products include food packaging, detergent containers, toys, and windows. Managing plastic waste properly is now crucial due to its contamination of the environment and food chain, leading to serious consequences. As noted in the Plastic Europe circularity report of 2022, immediate solutions are imperative [Plastic Europe circularity report, 2022]. Microplastics (MPs) are formed from the mechanical wear, UV degradation, and oxidation of plastic waste and are defined as tiny plastic particles ranging in size from 1 mm to 0.1 µm.
There are two types of MPs: primary and secondary. The primary category includes particles created for specific purposes such as skin treatment or cosmetics, while the secondary category includes particles resulting from the wear and tear of materials like packaging or clothing. A ban on intentional use of MPs in products that release microplastics was proposed in 2019. MPs have gained attention from the scientific community as environmental pollutants and a potential health concern, with recent studies focused on concentrations in marine environments, water, and seafood, but more research is needed on foods [Chem. Rev. 121 (2021) 11886–11936; Environ. Pollut. 231 (2017) 1256–1264].
Considering this, the aim of this study was to determine whether chocolate, collected during their packaging process, could release microplastics in the surrounding environment.
The samples were obtained using combined enzymatic and chemical degradation. They were deeply studied via micro-FTIR and micro-Raman spectroscopy analyses, in order to check the eventual presence of MPs.
From the results obtained, the presence of microplastics was evidenced. Particular attention was paid on polyethylene (PE), as packaging composition material.

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P-13

Automated, highly sensitive analysis of target residual fumigants in coffee by multi-step enrichment–headspace–trap (MSE–HS–trap) coupled with GC–MS for regulatory food safety testing

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Keywords: *Automation, Cryogen-free, Fumigants, Food safety, Headspace-trap*

Fumigation is a vital pre- and post-harvest process to prevent spoilage of foodstuffs from unwanted pests, bacteria and fungi. Fumigant compounds tend to have characteristics of being highly volatile and be able to dissipate through materials with ease, making them ideal for removal of any unwanted contaminants. However, these attributes come with high toxicity levels, leading to scrutiny of residues left behind. One of the most popular fumigants traditionally was bromomethane, but over time scientists discovered that this fumigant, and several halogenated compounds were depleting the ozone, leading to 'phasing out' of these substances. Known as the Montreal Protocol, this international treaty regulates the consumption and production of such substances, therefore robust testing is crucial for import/exportation companies.

Regulations of fumigants also go beyond just ozone depleting compounds, as in 2020, the European Union (EU) took action against another popular fumigant, ethylene oxide, where over 450 notifications were accumulated by the Rapid Alert System for Food and Feed (RASFF) [European Union Reg. (EU) 2015/868]. The notifications reported very high concentrations of ethylene oxide over the maximum residue limit (MRL) of 0.05 mg/kg, leading to thousands of product recalls across the EU. Therefore, stringent testing of fumigant residues has become a pivital requirement for importation and exportation of foodstuffs throughout the globe.

Here, a multi-step enrichment–headspace–trap method for the extraction of a range of fumigants was developed using the Centri 90 automated sample concentration system, coupled with gas chromatography–mass spectrometry analysis (MSE–HS–trap GC–MS). MSE–HS–trap exploits the use of the focusing trap to significantly enhance traditional headspace extraction. Using this technique, multiple headspace extractions are taken from the same vial and injected not to the GC inlet directly, but instead to an electrically–cooled, backflushed trap. The trap contains multiple sorbent beds of increasing strength, to retain and enrich a wide range of volatile organic compounds (VOCs). After the preconcentration step, the trap is subsequently purged and then rapidly heated (>100 °C/sec) in a reverse flow of carrier gas, desorbing analytes to the GC for separation and detection. Here, we show excellent results using this method, reporting MDLs as low as 0.0018 mg/kg for all fumigants, well below regulatory limits set out by the EU at 0.01 – 0.05 mg/kg. Excellent chromatographic performance was achieved, with linearity R^2 >0.99 and relative standard deviations <10% for all compounds indicating good reproducibility. Alternate matrices were also tested to validate the MSE–HS–trap method, whereby all fumigants were again, successfully extracted and analysed across the entire concentration range investigated. Full automation with prep-ahead functionality offered by Centri 90 provided an efficient, hands-free workflow with throughput of approximately 41 samples per system per day, ideal for high productivity, routine analytical laboratories.

P-14

Determination of steroid hormones adsorb on microplastics from the Macaronesia

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Keywords: *Hormones, Microplastics, Ultrasound, Chromatography*

Steroid hormones are a diverse group of endocrine disrupting compounds that can display lipophilic behaviour and, therefore, can be adsorbed on microplastics. Microplastics have become a significant environmental concern in marine ecosystems, as they pose harmful effects on exposed organisms. When the steroid hormones are adsorbed onto their surfaces, these effects are amplified. In this study, the presence of thirteen steroid hormones of several groups, androgens, estrogens, glucocorticoids and progestogens, is determined in microplastic samples collected from beaches in the Macaronesia region over a period of two and a half years. An ultrasound-assisted extraction (UAE) process followed by ultra-high performance liquid chromatography with tandem mass detection (UHPLC-MS/MS) was applied. Several of these pollutants were identified and quantified with concentrations in the range of $ng \cdot g^{-1}$. Mostly all concentrations obtained were from 18 to 200 $ng \cdot g^{-1}$, but in specific samples high concentrations were obtained even up to 897.71 $ng \cdot g^{-1}$.

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P-15

Assessment of the presence of synthetic hormones in stranded cetaceans

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Keywords: *Synthetic steroid hormones, Cetacean blubber, Stranded cetaceans, Ultra-high performance liquid chromatography-mass spectrometry*

The analysis of synthetic steroid hormones within cetaceans, offers a valuable information for evaluating the presence of contaminants in the ocean food chain. In this regard, blubber samples have been identified as a suitable matrix for this type of analysis. This article present a QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) extraction procedure combined with ultra-high performance liquid chromatography tandem mass spectrometry UHPLC-MS/MS analysis to determine the presence of synthetic steroids (1 androgen, 3 progestins and 2 corticosteroids) in blubber samples obtained from stranded cetacean. The tested methodology showed remarkable precision and recoveries ranging between 70 and 120% for most of the target compounds. Notably, all targeted compounds were detected in all samples, with megestrol acetate quantified in one of these. These results suggest that the potential of the methodology for the assessment of the presence of steroid hormones in cetacean tissue samples, contributing to a better understanding of the impact of these compounds on cetacean health and conservation.

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P-16

Determination of bisphenols, parabens, benzophenone-3 and triclosan in human urine by liquid chromatography coupled with tandem mass spectrometry

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Keywords: *Phenols, Urine, Liquid chromatography, Mass spectrometry*

Bisphenols, parabens, benzophenone-3 and triclosan are synthetic chemicals composed of hydroxyl-phenyl functional groups. These compounds are commonly used in various products such as cosmetics, pharmaceuticals, and food items. Due to their potential to disrupt the endocrine system, they have raised concerns among researchers and regulatory bodies.
To address the need for a reliable method to detect these compounds in human samples, a fast, sensitive, efficient, and high-capacity method was developed. This method allows for the accurate determination of them in human urine samples. By employing this method, researchers can analyse the presence and concentration of these chemicals in a timely manner, contributing to a better understanding of their potential impact on human health.
This strategy is based on incubation with β-glucuronidase/arylsulfatase followed by dilution in 96-well plates. The diluted samples were directly injected in a liquid chromatograph coupled with tandem mass spectrometer for their quantification. The ionization mode selected was electrospray in negative mode. During the method validation, the recoveries ranged between 80 and 120% with RSDs lower than 20% for all analytes using spiked levels from 0.2 to 200 $\mu g \cdot L^{-1}$. The limit of quantification was between 0.2-0.5 $\mu g \cdot L^{-1}$ and the linearity showed a $R^2 > 0.99$ in all cases.
The proposed method was successfully applied for the determination of those compounds in 10 urine samples of volunteer adults from the Valencian Region (Spain).

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P-17

PEsticide Reduction using Friendly and Environmentally Controlled Technologies: PERFECT LIFE project results

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Keywords: *Pesticides, Ambient air, Agriculture, Public health*

Control of pests and diseases in commercial crops is a permanent concern for farmers due to the important yield and economic losses. Pesticides play an important role in agricultural production, preventing disease and infestation of crops. In Europe, every year around 350.000 tons of pesticide-active ingredients are sold [Eurostat, 2022]. As expected, the countries with the highest pesticide use are those with the highest agricultural production like Spain, France and Italy, the 3 countries where the PERFECT LIFE project is working on.

PERFECT is a European project funded by the LIFE call of the European Commission that runs from September 2018 to August 2023. The main objective of this project is to demonstrate the reduction of pesticides in the environment using Optimal Volume Rate Adjustment (OVRA) tools and Spray Drift Reducing Techniques and Tools (SDRTs) during the applications, and improve the knowledge of stakeholders to achieve environmentally sustainable crop productions. Additionally, in the frame of the project, a new ultra-fast technology for the analysis of pesticides in the air is developed.

PERFECT LIFE is achieving its ambitious goal, of obtaining a general procedure for pesticide application with low emissions to the environment and protecting public health. Due to the use of SDRT and OVRA tools, pesticide consumption and emission is reduced, and in consequence, fuel saving, time saving and CO_2 emissions reduction are also achieved. More specifically, reductions of up to 74% of the volume used of phytosanitary product, and even saving fuel up to 800 liters and time up to almost 100 hours for every 100 hectares treated are observed. In citrus, the average pesticide volume reduction was 48%, and results show that exposure inhaled was reduced by 84%. In turn, biomarkers in urine were reduced by around 40% in this crop.

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P-18

Relevant hyphenated techniques to study volatile organic compounds for the development of biobased materials from seaweeds

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Keywords: *Emissions, Sargassum spp, Sample preparation, Chromatography*

Large concentrations of *sargassum* seaweed have been seen since 2011 throughout the Caribbean region, as well as in Central America, North America, and Africa. They decay when they run aground and remain on the shore, which significantly releases volatile compounds into the atmosphere, including aldehydes, sulfur and nitrogen compounds, among others. The kinetics of the emissions depend on the seaweed's state of decomposition, the types of compounds that are released, as well as the weather, particularly the temperature and the amount of precipitation. Among these substances, formaldehyde, ammonia, and hydrogen sulfide are known for being poisonous. *Sargassum* seaweed could potentially be given value by being included into biobased materials, particularly binderless particleboards. The resulting products can therefore be sources of emissions of some toxic compounds due to degradation of raw algae in new materials or during their use. It is therefore essential to control and quantify the atmospheric emissions of these materials in order to confirm their safety.
This study was first focused on the direct desorption of the raw material by pyrolysis-GC/MS, that provided a better understanding of the compounds released by *sargassum*. Then, emissions of materials were investigated using test chambers in dynamic mode which were subjected to controlled environmental conditions (temperature, hygrometry). Several sampling media as Tenax® TA, DNPH-coated solid sorbents coupled respectively with thermodesorption-GC/MS and HPLC-DAD analysis were used to study the emitted compounds. These relevant hyphenated techniques allowed to highlight key VOC emitted by sargassum-biobased materials which could be monitored during the development of the new materials.

P-19

Chemical speciation of cadmium in water samples by magnetic carbon nanotubes-based solid-phase microextraction

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Keywords: *Solid-phase microextraction, Magnetic carbon nanotubes, Trace metals, Natural waters, Chemical speciation*

The increasing pollution of the aquatic ecosystems with potentially toxic metals is a problem with a high environmental impact. However, the study and analysis of these metals in natural waters is hampered by the complexity of the matrix, specially in saline waters, and the very low concentrations in which they are found. For this reason, it has become important the development of analytical methods for the separation and pre-concentration of trace and ultra-trace metals in natural waters for their detection and quantification. Traditionally, liquid-liquid extraction (LLE) and solid-phase extraction (SPE) have been used for the determination of trace metals in water. Subsequently, the performance and environmental impact of these techniques have been improved by the miniaturization of the systems, giving rise to solid-phase and liquid-phase microextraction techniques (SPME and LPME). Within the SPE, we can highlight the use of carbon nanotubes (CNTs) due to their mechanical properties and nanometric scale. Moreover, functional groups can be incorporated into the structure of CNTs, improving the selectivity of the extraction of specific metals as well as the speciation studies on complex samples. In this way, CNTs have demonstrated to be promising candidates in the separation and preconcentration of metals in water samples. However, despite the advances made in SPE with CNTs, there are limitations and areas for improvement in relation to the difficulty of separating CNTs from the liquid sample after extraction, and the impossibility of reusing the CNTs. Here we propose the magnetization of several functionalized and non-functionalized CNTs with magnetic nanoparticles to separate them from the sample quickly and simply with an external magnet and their application to the SPE of metals in complex matrices. Thus, different magnetic materials based on CNTs with different diameters and functional groups have been prepared by using magnetic magnetite nanoparticles (Fe_3O_4). The prepared magnetic carbon nanotubes (MCNTs) have successfully performed the extraction and re-extraction of Cd in milliQ water highlighting the increased yield with the functionalized MCNTs than in the pristine ones, achieving Cd extraction rates of 99.8% for MCNT-COOH, 96.1% for MCNT-OH and 76.4% for MCNT in optimal conditions. Then, the presence of both organic and inorganic ligands was studied by using organic matter (humic acids) and NaCl. The results showed that Cd extraction was not significantly affected by the presence of organic matter but strongly affected by the salinity of the samples, suggesting the possibility of identifying the individual separation of cadmium chlorocomplexes. Hence, a Cd speciation study in saline samples was carried out by modelling calculations with the CHEAQS Next® software and Cd extraction experiments at different NaCl concentrations for the three selected MCNTs, observing that the decrease in the Cd extraction rates was co-related with the decrease of Cd^{2+} present in the samples.

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P-20

Multidetermination of benzophenone and derivatives in sunscreen by direct-immersion solid-phase microextraction and gas chromatography–mass spectrometry

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Keywords: *Direct-immersion solid-phase microextraction, Gas chromatography-mass spectrometry, Benzophenones, Sunscreen*

Benzophenones and their derivatives (BPs) compounds are widely used in sunscreen products as ultraviolet filters. As the awareness about the risks of sun exposure and its relationship with some skin cancers, personal care products containing these compounds has grown. The mechanism for protecting the skin consist of the formation of a thin layer on the surface of the skin, absorbing different wavelength from sun radiation. BPs can absorb ultraviolet light in the range of UVA (320-400 nm) and UVB (290-320 nm) [J. Chromatogr. A 1200 (2008) 260–263]. The target benzophenones were benzophenone (BP), BP-1, BP-3, BP-4, 4-MBP, 2,2',4,4'-tetrahydroxybenzophenone, enzacamene, 2,2'-dihydroxy-4-methoxybenzophenone, octinoxate, and dioxibenzone. The International Agency for Cancer Research (IARC) set that BPs alter the reproduction and hormonal function in fish. BP-1 has been addressed as 200 times more powerful in terms of estrogenic activity. IARC also classifies BP as possible human carcinogen in group 2B as it affects the liver and kidney of experimental animals [IARC. (2013). IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, No. 101. 2003].
Different approaches, in terms of pretreatment, are included in the literature for BPs extraction and isolation [J. Hazard. Mater. 430 (2022) 128495]. Typically, the first step in the pretreatment consists of dissolving the sunscreen lotion in a proper solvent. The main problem with this type of sample is the high matrix effect. A challenge in the scientific community is to reduce it while the extraction efficiencies of the procedure are kept high. Fats, glycerin, paraffin, and other high-complexity compounds and ingredients may easily be found in the matrix.
A methodology based on SPME in combination with GC-MS has been developed for the isolation and determination of BPs and its derivates in sunscreen products. Using very low volumes of organic solvents in comparison with other extraction techniques. The method was validated with good analytical properties: acceptable recovery, good linearity, and precision (relative standard deviations less than 8%) for the successful determination of the analytes in different sunscreen products at µg/kg level.

P-21

Assessment of chlorinated pesticide content in eggs and milk consumed in rural Roma communities in Transylvania, Romania, and their risk to human health

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Keywords: *Chlorinated pesticide, Gas chromatography, Eggs, Milk, Rural Roma communities*

The main purpose of this research is to evaluate the content of 22 chlorinated pesticides (OCPs) in eggs and milk consumed in some rural Roma communities in Transylvania, Romania, with the goal of estimating their risk to human health. A total of 26 eggs and 10 milk samples were collected from 14 rural Roma communities, either from local producers or from the local market. The OCP content was determined by gas chromatography and electron capture detector (GC-ECD). Prior to GC-ECD analysis, target compounds were extracted from egg and milk matrices by solvent extraction using a mixture of hexane:acetone (1:1 v/v), followed by defatting the extract with sulfuric acid and washing with sodium sulfate, according to a slightly modified method of Anwarul Hasan [NFS J. 27 (2022) 28–35]. The extraction recovery of the tested compounds varied between 78 and 110% for milk and between 72 and 96% for eggs, respectively.
In egg samples, the concentration of OCPs ranged from not detected to 0.311 µg/g. From 26 egg samples analyzed in 2 samples no OCPs were detected, in 10 samples the concentration was below 0.05 µg/g (maximum residue limits (MRLs) of pesticide residues in eggs) and in 14 samples the OCP concentration exceed the MRL.
The most OCPs found were Endrin (22 samples, from 0.012 to 0.28 µg/g), Heptachlor (10 samples, from 0.002 to 0.08 µg/g), alpha-endosulfan (8 samples, from 0.008 to 0.099 µg/g), Heptachlor epoxide (2 samples, from 0.007 to 0.014 µg/g), trans-chlordane (1 sample, 0.018 µg/g), and 4,4'-DDE (1 sample, 0.02 µg/g).
No OCPs were detected in the analyzed milk samples.
The estimated daily intake (EDI), hazard quotient (HQ) and hazard index (HI) were used to assess human risk and exposure to pesticide residues from milk and egg consumption.
The concentration of pesticides such as ∑DDT, ∑Endosulfan, Endrin, ∑Heptachlor, average daily egg consumption and average adult body weight were considered to calculate the EDI.
EDIs range from 1 to 32 for ∑Heptachlor, 5 to 112 for Endrin, 3 to 40 for ∑Endosulfan, and 8 for ∑DDT. HQ values ranged from 0.001 to 0.032 for ∑Heptachlor, from 0.051 to 0.1125 for Endrin, from 0.035 to 0.039 for ∑Endosulfan, and 0.008 for ∑DDT.
HI values ranged from 0.0045 to 0.116, values that are below 1 and considered acceptable and safe for human consumption.

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P-22

Towards a high efficiency electromembrane system for cadmium analysis in water at sub-ppb levels

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Keywords: *Electromembranes, Cadmium, Water, Sample preparation, Microextraction*

Sample preparation is the most time consuming step to determine metals in water at sub-ppb levels. Usually, metals must be extracted from the sample to a simpler aqueous solution by a liquid extraction with an organic solvent or a solid extraction with an adsorbent. In this case, extraction and re-extraction steps are often required and the complete process can be very laborious. Then, most of the efforts have been made to get the most efficient methods without loss of accuracy and precision and also minimizing the risk of contamination. All of these aspects are providing by electromembranes, where an electric potential is applied to a hollow-fiber liquid-phase microextraction system with the main objective of accelerating the extraction process. In addition, a three phases configuration with the pores of the fiber filled with the organic solution and the lumen filled with the re-extraction solution, allows to perform extraction and re-extraction processes simultaneously.

In this work, an electromembrane system for cadmium analysis in water samples has been developed based on a previously optimized hollow-fiber liquid-phase microextraction system to preconcentrate cadmium from water samples. In this system, a three phases configuration with a solution of Cyanex 272 in 1-octanol in the pores of the fiber and a nitric acid solution in the lumen of the fiber has been used. To configure the electromembrane system, two platinum electrodes (0.25 mm thick) connected to a power supply for the application of an electric potential were used. One electrode, the cathode, was immersed into the sample and the other one, the anode, into the acceptor solution inside the lumen of the hollow-fiber. Then, several preliminary experiments were carried out to establish the effect of the organic phase and the electric potential (0-250 V) on the extraction efficiency. From the results, a positive effect was observed when electric potential increased using 1-nonanol as solvent in the organic phase. Later, the electromembrane system was optimized to obtain the best extraction efficiency.

For optimization, the modified Simplex method, a sequential-evolutionary optimization methodology, was used to take into account the interaction between the different factors affecting the extraction processes. The factors to be optimized were the sample pH, the electric potential, the extractant concentration and the re-extractant concentration. A reference value of 5, 50 V, 0.05 M of Cyanex 272 and 0.2 M of nitric acid and a step size of 2, 150 V, 0.2 M and 1 M was selected, respectively, to calculated the initial simplex. All experiments were performed for an extraction time of 15 minutes, to prevent the Joule effect, and a stirring rate of 350 rpm. After seventeen experiments the simplex was stopped following the criterion of variance and an optimum enrichment factor of 26.6 ± 4.4 was obtained for a sample pH of 6, an electric potential of 180 V, a Cyanex 272 concentration of 0.05 M and a nitric acid concentration of 0.2 M.

After that, the effect of extraction time and stirring rate was also investigated, achieving an enrichment factor of 108.32 ± 10.33 for 30 min and 1300 rpm. Besides, the effect of sample salinity was also evaluated and a negative linear relationship between the logarithm of enrichment factor and Cl^- concentration was obtained.

Finally, the system was applied to the analyses of five non-saline real samples added with 30 and 50 $\mu g \cdot L^{-1}$ of cadmium. The recoveries were dependent on the chlorides concentration in the samples.

P-23

Extraction and analysis of phenolic compounds in *Phaeodactylum tricornutum* cells in Cu polluted cultures

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Keywords: *Phenolic compound, Copper toxicity, Phaeodactylum tricornutum, Antioxidant activity*

Organic compounds produced by phytoplankton can regulate speciation, bioavailability, and toxicity of metals in the cells and medium. Copper (Cu) is an essential micronutrient for microalgae that becomes toxic at certain concentrations. The presence of harmful levels of this metal in coastal waters due to human activities or natural activities like volcanic episodes can cause severe damage to microalgal cells. The accumulation of organic metabolites by microalgae can be considered as a defense mechanism of the algae to overcome metal toxicity. Phenolic compounds are characterized by their antioxidant capacity, protecting the cells of microorganisms from oxidative damage.

The aim of this study is to characterize the phenolic material accumulated by the diatom *Phaeodactylum tricornutum* and its antioxidant activities. For this purpose, *P. tricornutum* was cultivated under seawater and seawater with 0.31, 0.79 and 1.57 µM of Cu(II) and polyphenols and were analysed after 12 and 18 days. The determination of 10 different polyphenols was carried out by reverse phase high-performance chromatography with photodiode array detector. The stress conditions of the diatom cells were confirmed by malondialdehyde determination and the antioxidant activity by the cupric ion reducing assay.

Increasing levels of Cu in the medium produce an accumulation of polyphenols up to 11.3 times higher than cells cultured without Cu. The cupric ion reducing antioxidant capacity and malondialdehyde content exhibited the same tendency. These results confirm that under Cu toxic conditions, the diatom cells synthetized phenolic compounds as a protective mechanism against oxidative stress produced by the presence of heavy metals as Cu.

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P-24

Determination of residues of pharmaceutical active compounds in water samples – Optimization of the analytical method

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Keywords: *Water, Emerging pollutants, Pharmaceutical residues*

Modern multi-residue methods based on liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) can be used for determination of hundreds of micropollutants from different chemical classes as well as their metabolites in many matrices, including environmental samples (emerging pollutants). The aim of the research was to develop and validate a multiresidue method for monitoring surface and groundwater at the lowest possible levels, covering active substances of pharmaceuticals (Pharmaceutical Active Compounds – PhACs). For the study 10 different PhACs were selected i.e. carbamazepine (antiepileptic), diclofenac (nonsteroidal anti-inflammatory), fluconazole (antifungal), gabapentin (antiepileptic), lamotrigine (antiepileptic, antidepressant), paracetamol (analgesic), sulfamethoxazole (human and veterinary antibiotic), sulphapyridine (antibacterial), telmisartan (treatment of high blood pressure) and tramadol (analgesic). All PhACs certified reference materials were characterized by >99% purity. Carbamazepine-D10 was used as an internal standard.
The method validation was carried out according to the SANTE/11312/2021 guideline. The recovery tests were performed by spiking blank samples of water with a solution of PhACs at 0.01, 0.025 and 0.1 µg/dm³ levels. Modular QuEChERS extraction method (Norm EN-15662:2018) was used to isolate the analytes and remove the impurities. Finally, the aliquot of extract was evaporated to dryness and diluted in LC-MS/MS mobile phase prior to the instrumental determination. The described method of isolation the pharmaceuticals from water is very simply, complicated and time-consuming analytical steps are avoided.
In the study, development and validation of a multi-residue method for pharmaceutical residues determination in water were performed using LC-MS/MS ultra performance liquid chromatograph (Waters Corp. Acquity UPLC system) interfaced with a mass spectrometer equipped with an electrospray ionization source operated in the positive mode (AB Sciex, Qtrap 6500, EI+ mode), chromatographic separation - Atlantis C_{18} (100 mm × 2.1 mm, 3 µm) column (Waters Corp.) and buffered water/methanol phases in gradient mode. Ionization and MS/MS collision energy settings were optimized while continuously infusing PhACs solution via a syringe pump. For each pharmaceutical, the parent and two or three of daughter ions were selected and the first one was used for quantification and the others for confirmation. Data acquisition and the quantitative analysis was based on the multiple reaction monitoring (MRM) technique.
Recoveries of the all of compounds tested were in the 70–120% range and were characterized by precision lower than 20%. The high sensitivity of the method allowed the successful determination of all the compounds at the level of 0.025 µg/dm³ or lower. The developed, validated and optimized method was used in the analysis of water samples of the Warta River during the Covid-19 pandemic (12 sampling campaigns, March 2020 – April 2021). Sampling points were located in the urban section of the river (the city of Poznań). All selected PhACs were detected in water samples during the tests at the various concentrations ranged from 0.02 to 7.5 µg/L.

P-25

An analytical method to quantify volatile methylsiloxanes from microplastics

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Keywords: *Volatile methylsiloxanes, Microplastics, Solid-liquid extraction, Gas chromatography coupled with mass spectrometry, Green analytical chemistry*

Microplastics are a global concern for some time now, as their ubiquity places them in virtually every compartment of the Earth's environment and ecosystems. Apart from being contaminants themselves, they can also act as vectors for other pollutants, given their ability to adsorb and release them depending on the surrounding conditions. Volatile methylsiloxanes (VMSs) are also ubiquitous anthropogenic substances that have extraordinary properties for use in numerous industrial and consumer products. The production of plastics can also benefit from VMSs and their semi-volatile organic nature makes them prone to adsorption to materials such as microplastics in the environment.

To this day, no study focused on the analysis of VMSs in microplastics, so we optimized and validated a methodology based on solid-liquid extraction aided by sonication, aiming the further quantification in naturally contaminated microplastic particles collected in beaches. The following common commercial microplastics were tested: polypropylene (PP), polystyrene (PS), high-density polyethylene (HDPE) and low-density polyethylene (LDPE), as they are typically found in coastal areas. Several extraction solvents were tested with each microplastic type individually (hexane, acetone, ethyl acetate and hexane:dichloromethane 1:1). Acetone was selected and the following tests (sample mass, solvent volume, number of extractions, vortex/ultrasound duration, adding a QuEChERS clean-up) were performed with one quarter of each microplastic type to maximize the recoveries. The final method included a filtration step instead of the QuEChERS approach to clean the final extracts.

The method detection and quantification limits (MDL and MQL) ranged from 0.0003 to 0.23 ng/g and from 0.0007 to 0.77 ng/g, respectively. The accuracy and precision were assessed at two VMS spike levels (100 and 500 ng/g). The mean recoveries were 84% at 100 ng/g and 94% at 500 ng/g, the mean repeatability was 9% at 100 ng/g and 6% at 500 ng/g, and the intermediate precision was 6% at 100 ng/g and 2% at 500 ng/g.

In field samples, this method was able to quantify total VMS levels up to 122 ng/g in some microplastics collected in beaches, with a clear predominance of the cyclic compounds. This expedite and green method can thus be used to assess the presence of VMSs in microplastics and assess the potential of the latter to act as carriers of the former in future studies.

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P-26

Extraction and derivatization of arsenic trichloride and arsenous acid in water and soil samples for gas chromatography coupled with mass spectrometry analysis

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Keywords: *Arsenic trichloride, Soil samples, Extraction, Derivatization, Gas chromatography-mass spectrometry*

DGA CBRN Defence is one of the designated laboratories by the Organisation for the Prohibition of Chemical Weapons (OPCW). One of its missions is to characterize the risk associated to Chemical Warfare Agents (CWA) and to participate to the analyses in case of alleged use of such chemicals during a specific event. The unambiguous identification of these compounds in environmental matrices has to be performed by using at least two different analytical techniques. OPCW criteria require detection limit of 1 ppm during Interlaboratory Proficiency Tests.
Arsenic trichloride is a precursor of Lewisites (CWA), and is therefore a Chemical Weapons Convention (CWC) scheduled chemical (code 2.B.07). Due to its chemical properties (corrosive and reactive), arsenic trichloride, in its native form, cannot be analyzed by gas chromatography coupled with mass spectrometry (GC-MS) and must be derivatized by a thiolation or silylation process. Arsenic trichloride, mainly present in organic samples and its degradation product, arsenous acid ($As(OH)_3$), mainly present in water or soil samples, cannot be distinguished after derivatization. Indeed, the same derivatized chemical is formed and analyzed by GC-MS.
The protocol described in the Recommended Operating Procedures (ROP 2017) written by the experts of OPCW designated laboratories for the GC-MS analysis of Lewisites has been applied in water and soil samples, which were spiked by $AsCl_3$ at 1 µg/mL and 1 µg/g respectively. Nevertheless, this ROP protocol was not conclusive for the thiolation of $AsCl_3$/$As(OH)_3$ in water and in an aqueous extract obtained by soil extraction. Water soil extraction was achieved either by sonication or by accelerated solvent extraction (ASE).
During this study, the derivatization process was optimized in an aqueous sample by comparison of 4 protocols. Then, the optimized protocol was successfully applied to an aqueous extract of a soil spiked by $AsCl_3$ at 1 µg/g level (1-propanethiol derivatization step on the aqueous extract followed by organic extraction and 1-propanethiol derivatization step on the aqueous residue).

P-27

Evaluation of the occurrence of pesticides and their transformation products associated with olive groves in surface waters using UHPLC-Orbitrap-MS suspect screening

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Keywords: *Pesticides, Transformation products, Mass spectrometry, Suspect screening*

Most natural waters are subjected to contamination by anthropogenic chemicals. In rural areas, where the primary sector is predominant, one of the principal causes of the contamination of natural waters is the use of pesticides. The province of Jaén, located in the southeast of Spain, accounts for more than 588,000 ha dedicated to olive groves. These crops are mainly managed using conventional practices that involve the application of plant protection products or pesticides. These compounds, along with some of their transformation products (TPs), may be discharged to water bodies of the Guadalquivir river basin.
In this study, a suspect screening strategy by UHPLC-Orbitrap-MS was developed to identify pesticide residues and their TPs, complementing a target method. This approach was based on the use of public databases and market data to compile a suspect list of more than 500 pesticides and their TPs. The automatic processing parameters included several steps to filter the number of potential candidates, such as $[M+H]^+$ mass accuracy (≤ 5 ppm), isotopic pattern fit (M+1 and M+2 mass accuracy error ≤ 5 ppm), and a spectral match of the acquired MS/MS spectra with reference spectra in libraries (≥ 80% score).
This strategy was successfully applied to retrospectively analyze 27 water samples collected from 11 sampling points of the Guadalquivir river and some of its main tributaries over 2 years of monitoring. A total of 6 compounds were tentatively identified with high-confidence level, which included 1 pesticide and 5 TPs. A semi-quantification methodology was also applied to evaluate the concentration levels of the newly identified compounds.

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P-28

Optimizing the solvent extraction of soil lipid components related to the organic matter hydrophobic character

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Keywords: *Soil health, Hydrophobicity, Water repellency, Organic matter, Ultra-high performance liquid chromatography-diode array detection*

The European Union (EU) has proposed five missions to bring concrete solutions to some of our greatest challenges: i) adaptation to climate change, ii) cancer, iii) ocean and waters, iv) climate-neutral and smart cities, and iv) the transition towards healthy soils. “Caring for soil is caring for life” is the title of the mission proposed by the European Commission (EC) whose goal is to ensure that, at least, 75% of soils in each EU member state are healthy by 2030 and are able to provide food and other biomass, support biodiversity, store and regulate water flow or mitigate climate changes. Soil health is defined as the continued ability of the soil to function as a vital ecosystem that supports plants, animals and humans. Because of the diversity of its components and phases and its multifunctionality, soil is a very complex system; for this reason, the physical, chemical and biological properties of the soil must be taken in consideration to understand the phenomena that characterize its health. Soil aggregation is a dynamic phenomenon that affects the retention and movement of water, gaseous exchange and mechanical properties as well as germination, root growth, compaction and erosion. The development of stable soil aggregates depends on: i) both the nature and content of organic matter, ii) sand, silt, and clay content, iii) nature of clay minerals, iv) microbial populations and their activity, and, to a lesser extent, v) abiotic factors. Knowledge concerning the influence of the various components of soil organic matter (SOM) on the stability of soil aggregates is crucial. The decomposition of SOM yields increasing proportions of long-chain aliphatic compounds and decreasing proportions of polysaccharide materials. Soil lipids are heterogeneous material composed of linear and nonlinear, polyfunctional compounds of different reactivity. Besides, it has been described that the hydrophobic fraction extracted from soil with n-hexane contributes to the water stability of soil aggregates, but the nonextractable and more reactive fraction of the soil lipids appears to be involved in the more permanent stability of soil aggregates.
The aim of this study was to stablish the optimal conditions for obtaining extracts with high content on hydrophobic compounds from soil. To this end, how variables such as soil weight-to-extractant volume ratio and extraction time (ranging between 1:5 and 1:50 w:v and between 0.5 and 3 hours, respectively) influence the extraction process was studied. Other factors implicated in the extraction were kept constant: type of extractant (n-hexane), extraction temperature (69 ºC) and number of extraction steps (3). The lipid components extracted were separated by ultra-high performance liquid chromatography and diode array detection (UHPLC-DAD), by using a linear acetonitrile gradient in water. The results suggest that both factors significantly affected obtaining extracts with high content on SOM components with hydrophobic properties, being the soil weight-to-solvent volume ratio the most important. For a fixed extraction time, decreasing the weight-to-volume ratio from 1:50 to 1:5 (w:v) led to an increase of the number of extracted components, from 10 to 18. Moreover, the amount extracted for most of the components increased 7-17 times for the lowest soil weight-to-extractant volume ratio evaluated. Therefore, a ratio of 1:5 (w/v) was selected as the optimum value of this factor. Regarding extraction time, in general, extraction of hydrophobic compounds from soil kept constant between 0.5 and 2 hours, decreasing the amount of extracted components when the time was increased to 3 hours. Under the optimized extraction conditions, three soils with different health conditions were sampled in the Canary Islands (Spain) and characterized by using their lipid components related to the SOM hydrophobic character, water repellency, sand, silt and clay content, total and oxidizable SOM, extracted SOM amount, cation exchange capacity, electrical conductivity and pH.

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P-29

Polymer inclusion membranes (PIMs) for the screening of metal pollution in natural waters

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Keywords: *Polymer inclusion membrane, Metals, Screening, Preconcentration, Natural water*

Nowadays, there is a clear requirement for simple and efficient techniques for the screening of metal pollution in natural waters. Passive samplers are useful for detecting contaminants in aquatic systems because they can measure the average concentration of pollutants over time (known as time-weighted average or TWA). By using passive samplers, the need to analyze a large number of individual samples, as required in spot sampling, is reduced. This approach saves time and costs while effectively detect pollutant levels in water.

In our study, we are investigating the use of new passive samplers based on polymer inclusion membranes (PIMs) for the detection of divalent metals in river waters. PIMs are a type of functionalized membranes made of an extractant embedded in a polymeric matrix, and have shown to facilitate the detection of metals such as Hg [J. Hazard. Mater. 371 (2019) 316–322] and organic compounds [J. Membr. Sci. 492 (2015) 32–39] in natural waters. Based on our previous results on Zn and Cu complexation [Appl. Sci. 11 (2021) 10404], we use a PIM made of 50% cellulose triacetate (CTA) as the polymer, 40% of di(2-ethylhexyl) phosphoric acid (D2EHPA) as the extractant, and 10% of 2-nitrophenyloctyl ether (NPOE) as the plasticizer to be incorporated in a special device able to be deployed on-site in a river. A 0.01 M HNO_3 solution was used as a receiving phase, where the extracted metals accumulate and are measured once in the laboratory with the appropriate instrumentation.

We have conducted multiple screening studies in five rivers located in North-East Catalonia (Spain) using PIM-devices. These devices were deployed in a net at designated sampling points for a duration of 24 hours. While the detection of metals was insignificant in four of these rivers, the PIM-devices deployed at a specific spot in the Osor River exhibited significant accumulation of zinc. This river is affected by continuous metal inputs from a disused mine, resulting in higher Zn concentration levels compared to the other rivers studied. Therefore, we conducted a sampling campaign at various points along the river to assess the dispersion of metallic pollutants throughout its course.

The obtained results demonstrate that PIM-devices are a simple and efficient tool for the screening of metal pollution in river waters.

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P-30

Effective removal of N-nitrosodiphenylamine from aqueous media using dead leaves of seagrass as a low-cost adsorbent

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Keywords: *Nitrosamines, Adsorption capacity, Removal efficiency, Water treatment, Reusability*

N-Nitrosodiphenylamine is a type of nitrosamine that is both highly soluble in water and extremely toxic. Even at low concentrations, long term exposure to N-nitrosodiphenylamine can result in a variety of health effects. As a result, removing N-nitrosodiphenylamine from aqueous samples using a widely available and cost-effective adsorbent is extremely challenging. In this work, without any chemical modifications, a highly efficient, eco-friendly, and low-cost biosorbent was prepared from the dead leaves of seagrass. The seagrass adsorbent was characterized and tested for the removal of the highly water soluble and toxic N-nitrosodiphenylamine from aqueous solutions. We investigated and optimized the effects of solution pH, contact time, adsorbent dosage, and adsorbate concentration. SG adsorbent removed N-nitrosodiphenylamine from wastewater solution with 83% efficiency using 1 $g \cdot L^{-1}$ of adsorbent. At neutral pH and room temperature, the maximum adsorption capacity of seagrass was found to be 64.84 $mg \cdot g^{-1}$. The results of the adsorption isotherm were fitted with the Langmuir model and followed pseudo-second-order kinetics. According to the thermodynamic parameters, the adsorption of N-nitrosodiphenylamine onto seagrass adsorbent is favorable, endothermic, and the chemical adsorption mechanism is dominant. According to the findings of this study, seagrass adsorbent is reusable and can be easily regenerated and reused at least three times with a slight decrease in removal efficiency.

P-31

Application of TD/Py-GCxGC-TOFMS for analysis of microplastics & chemical pollutants in ambient particulate matter samples

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Keywords: *Microplastics, Ambient air, Particulate matter, Gas-chromatography, Pyrolysis*

Microplastics are a widespread and abundant environmental pollutant and there is a growing interest in understanding human exposure and subsequent impacts on health. A major knowledge gap is exposure concentrations in air. Here, we describe the application of thermal desorption (TD) and pyrolysis (Py) coupled to multidimensional gas chromatography-time-of-flight mass spectrometry (GCxGC-TOFMS) to analyse the composition of plastics and chemical pollutants in ambient particulate matter (PM), collected via aerodynamic size selective sampling (<10 µm) at various urban locations. Specifically, a 2-step analysis of each sample was applied using firstly TD to measure, “free” or “associated” chemicals, and then secondly using Py to analyse and differentiate chemicals derived from microplastic particles, as strongly adsorbed or as thermal degradation species. This methodology was also used to assess the suitability of the sample collection and sub-sampling workflows by processing the data using ChromaTOF Tile statistical comparison software.

P-32

A sampling platform incorporating 3D-printed paddles-stirrers coated with metal-organic framework MIL-100(Fe) for *in-situ* extraction of phenolic pollutants in biodigester supernatant and wastewater effluent samples

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Keywords: *Portable 3D-printed stirrer, Solid-phase extraction, Metal-organic framework, Phenols, Wastewater*

Phenols are a group of hazardous organic pollutants widely distributed in the environment. Chlorophenols (CP) and nitrophenols (NP) come from domestic, industrial, and agricultural activities, and include pharmaceuticals, dyes, pesticides, plastics and refinery products. These compounds are highly persistent and cumulative in the environment and represent a carcinogenic risk to humans. Therefore, most of them are classified as priority pollutants by the United States Environmental Protection Agency (U.S. EPA) and European Union. On the other hand, bisphenol A (BPA) is an emerging pollutant and a wellknown endocrine disruptor, coming from production of plastics. In general, phenolic pollutants can deteriorate the effluent quality of a wastewater treatment plant because, at specific concentrations, they are toxic for anaerobic microorganisms that participate in the biological treatment of wastewater, turning out to be key inhibitors of methane production in the anaerobic digestion.

In this work, we propose a portable, simple and low-cost paddle stirrer for solid-phase extraction of phenols (4-NP, 2-CP, 4-CP, 2,4-DCP, 2,4,6-TCP, PCP and BPA) from wastewater samples. The platform consists of a small 3D-printed paddle stirrer attached to a small electric motor assembled on the lid of a jar (sample reservoir) and powered by a portable battery. The paddles of the stirrer were coated with metal-organic framework MIL-100(Fe), to be used as adsorbent for the simultaneous extraction and preconcentration of phenols. This material was prepared in 10 min using a green microwave-assisted synthesis. Once the stirrer is submerged in the sample, the motor is turned on to carry out the extraction procedure. The proposed sampler can be applied for in-situ extraction of the analytes, avoiding the transport of samples to the laboratory and allowing more accurate and precise results. Only the extractive phases are taken for ultrasonic desorption before analysis by HPLC-DAD.

An exhaustive study of the effect of the stirring (stirrer geometry, sampling depth, and stirring speed) and extraction parameters (desorption solvent, desorption time, sample volume, extraction time, pH and ionic strength) was carried out. To select the most suitable MOF immobilization technique, the Stick & Cure, the post-printing and a combination of the two techniques were tested.

Under optimum conditions, the detection limits were in the range from 0.3 to 1.7 $\mu g \cdot L^{-1}$ and, the precision as relative standard deviation obtained intraday and interday ranges between 1.2 and 5.1%, and 4.5 and 6.8%, respectively. The accuracy, evaluated using spiked samples of wastewater effluent and biodigester supernatant, provided relative recoveries in the range of 91.5–108.5%. The device is capable of extracting both, low and high concentrations of phenols (87.7–100%), and therefore also has potential for the removal of organic contaminants for wastewater remediation.

On a large scale, the device could also have a positive performance for water purification. The proposed platform shortens the analyst's work time since it allows the integration of the sampling and the extraction of the analytes in a single step. The stirrer is inexpensive, easy to build, and easy to use. To the best of our knowledge, this is the first work in which the paddles of a 3D-printed stirrer are coated with an adsorbent.

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P-33

Extraction of proteins with dendronized magnetic nanoparticles

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Keywords: *Protein extraction, Magnetic nanoparticles, Carbosilane dendrimers*

Extraction/purification of proteins requires the use of polluting solvents/reagents and high extraction times and temperatures. Moreover, these processes result in low selectivity and extraction rates. New extraction techniques have emerged as sustainable alternatives although, in many cases, they do not guarantee a 100% recovery of proteins. At this regard, the development of new nanomaterials provides additional opportunities to improve the extraction of proteins [Sep. Purif. Rev. 49 (2020) 229]. Magnetic nanoparticles (MNPs) have important characteristics that make them to be very interesting for the sustainable extraction of proteins, mainly, paramagnetism properties and easy functionalization. Indeed, the modification of their surface with appropriate ligands, e.g. multivalent ligands, could improve the extraction of proteins. On the other hand, dendrimers are globular molecules with branches, called dendrons, organized in layers. Main features of dendrimers and dendrons are their multivalent surface and capability to interact with biomolecules. MNPs functionalized with carboxylate-terminated carbosilane dendrons have been successfully employed to recover proteins from food by-products showing a high extraction rate and being possible their reuse [Anal. Bioanal. Chem. 414 (2022) 1677]. This work proposes to extend this first work by studying the ability of MNPs covered with multifunctional carbosilane dendrimers (CBS) for the extraction and purification of proteins.
Lysozyme (LYS), myoglobin (MYO), concanavalin (CONC), and bovine serum albumin (BSA) were chosen as protein targets due to their different molecular weight and isoelectric point. MNPs based on magnetite (Fe_3O_4) were synthesized with dendritic CBS systems modified with different functional groups (NH_2, OH, CO_2H, SO_3). The interaction between coated MNPs and proteins was analyzed taking into account the type of protein, dendrimer functional group, pH, and MNP:protein ratio (10:1 and 100:1). The results were compared with the obtained when using pristine iron oxide MNP. Further analysis of proteins release and MNPs recyclability were also carried out.

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P-34

Dyes and solvents in pen inks: Analytical methods for solving court cases

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Keywords: *Inks, Dyes, Solvents, Chromatography, Document dating, Forensic*

To know the date when ink from a pen was deposited on paper could be crucial in judicial processes that require proving the authenticity of a particular document. In judicial and expert analysis, it is common for the resolution of a particular case to require analytical techniques, specifically chromatographic methods, rather than optical or handwriting analysis techniques.
Once ink from a pen is deposited on paper, its composition gradually changes, with the concentration of the original compounds present varying. Solvents evaporate, reducing their concentration, while dyes degrade over time, resulting in the appearance of various degradation compounds [Microchem. J. 138 (2018) 550–561]. The first process occurs at a much faster timescale than the second, with more volatile solvents evaporating within days or weeks, while the degradation of certain dyes can take years.
To compare whether the analytical results coincide with the date recorded on the document, the extraction of 4 to 8 microdiscs (1.25 mm each) containing the ink sample from the questioned document is performed [J. Anal. Chem. 76 (2021) 660–670]. These microdiscs undergo solid-liquid extraction (with methanol), and the extract is simultaneously analyzed by HPLC-DAD-FLD and GC-MS [J. Chromatogr. A. 1515 (2017) 187–195]. Solvents and degradation compounds from more volatile dyes are analyzed by GC-MS, while less volatile compounds are analyzed by HPLC.
Reference samples with up to 10 years of aging were analyzed to establish correlation matrices and regression models between the concentration of each analyte and the time elapsed since the ink deposition. These reference samples were compared with actual judicial cases with a known date, demonstrating the validity of the method.

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P-35

Improvement of the saponification process for mineral oil analysis using microwave-assisted saponification/extraction

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Keywords: *Microwave-assisted saponification/extraction, Mineral oil hydrocarbons, Food analysis*

Mineral oil hydrocarbons are a group of contaminant considered possibly toxic, especially the MOAH fraction composed of aromatic compounds, mainly alkylated. The analytical determination is however linked to a lot of variability among them mainly the sample preparation, when enrichment and purification is needed, and the chromatogram interpretation. Recently, work has been done to automate more the chromatogram interpretation thus reducing the variability.
However, regarding the sample preparation, two interlaboratory trials done last year (JRC for infant formula and DGF for oil and fat) pointed to the difficulty of having a low sensitivity, the LOQ reaching 2 mg/mL for the MOAH fraction in fat samples due to a lack of reproducibility. One of the issue highlighted was the discrepancy in the recovery of the internal standards. Indeed, in both cases, TBB has a greater recovery than the MN standards with an average ratio of 1.15 instead of 1. The problem was that in one case, the recovery results were better using TBB and in the other using 2MN, suggesting that the contamination itself could have different recovery depending on its composition. In order to reduce this variability, a new saponification method was developed using microwave-assisted saponification/extraction and testing the partition of the internal standards in different matrices and conditions. In conclusion, the ratio discrepancy was reduced from between 1.11 and 1.18 to between 1.02 and 1.08 for all the matrices tested.

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Synergistic combination of green technologies for antioxidant phenolic compound extraction from orange by-products

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Keywords: *Antioxidant capacity, Enzyme-assisted extraction, Orange by-products, Phenolic compounds, Ultrasound-assisted extraction*

Fruit and vegetable processing is one of the agro-food industries that generate more amount of waste. For instance, in the citrus industry, around 50-60% of the total weight of the fruit is discarded, their elimination resulting in substantial economic costs. However, orange by-products can constitute a source of compounds with high added value and energy. They contain a great amount of biologically active secondary metabolites such as phenolic compounds. However, the recovery of bioactive compounds from these by-products presents a significant challenge, often requiring energy-intensive processes and the use of non-environmentally friendly organic solvents. This study presents a novel approach for extracting antioxidant phenolic compounds from orange (*Citrus sinensis*) pomace by combining sustainable extraction techniques, namely ultrasound-assisted extraction (UAE) and enzyme-assisted extraction (EAE). The efficiency of phenolic compound extraction from the orange pomace matrix was evaluated by comparing UAE-EAE combination with the individual use of UAE or EAE. Several enzymes were tested, Depol and Promod being selected as the most promising for the extraction process. Box-Behnken experimental designs were employed to determine the optimal conditions for UAE-EAE, including enzyme concentration (50-100 µL/g), ultrasound amplitude (30-60%), buffer pH (6.00-10.00), and extraction time (1-15 min). The total phenolic content (Folin-Ciocalteau method), proanthocyanidin content (DMAC and HCl/butanol assays), and antioxidant capacity (ABTS, DPPH, and hydroxyl radical scavenging assays) were measured. The optimal conditions for UAE-EAE with Promod enzyme were an enzyme concentration of 100 µL/g, 30% amplitude, pH 8.4, and 1 min extraction time, and an enzyme concentration of 100 µL/g, 30% amplitude, pH 8.0, and 8 min extraction time for Depol enzyme. Additionally, the phenolic compounds present in the optimal extracts were analyzed using HPLC-DAD, being identified flavanones as the main phenolic group. The optimal extraction conditions using UAE-EAE were compared with conventional extraction methods, revealing that EAE-UAE was a suitable extraction method to obtain phenolic compounds from orange pomace, resulting in extracts with higher proanthocyanin content and antioxidant capacity compared to conventional extraction methods.

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P-37

A new approach to sample preparation in electroanalytical methods: Nitro compounds adsorbed in a MWCNT bucky paper electrodic platform

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Keywords: *Carbon nanotubes, Buckypaper electrode*

Sample preparation represents one of the crucial steps in the chemical analysis procedure. In electroanalytical techniques, the sample is mostly incorporated by dissolution in a solution; however, this procedure leaves out samples that are insoluble or very slightly soluble. For a few years we have developed a technology that allows us to incorporate the electroactive compound into a carbon nanotube platform (CNT) and in that state perform the electroanalytical determination. Specifically, it is possible to carry out the study of very slightly soluble compounds adsorbed on the CNT platform and then to study the pH behaviour in that adsorbed state when introducing it into the corresponding buffer [J. Solid State Electrochem. 22 (2018) 1423–1429]. More recently, the technique has evolved and we prepare buckypaper (BP) with multi walled carbon nanotubes (MWCNT) and polystyrene, generating disc-shaped electrode platforms where the slightly soluble compound is incorporated by adsorption. Then, we introduce that electrode platform in solution to carry out the electrolysis and corresponding analytical determination [Electrochim. Acta 443 (2023) 141984].
The sample preparation procedure consists of weighing MWCNTs and polystyrene and then dispersing it in dioxalane, this dispersion is homogenized by sonication and continuous stirring until a homogeneous dispersion is obtained, which is filtered on a nylon filter paper, forming a BP disc. The BP is dried to remove traces of dioxalane and then cut to the desired size. The filter paper is cut using a paper cutting machine into discs with a diameter of 6 mm to modify the glassy carbon (GC) electrodes and 4.5 mm in diameter for the modification of screen printed (SP) electrodes.

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P-38

Aptamer-functionalized 3D-cylinder-shaped printed devices for in-vial microextraction of β-lactoglobulin prior to capillary electrophoresis-mass spectrometry

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Keywords: *Allergenic proteins, Aptamer, Capillary electrophoresis, Mass spectrometry, 3D-printing*

The analysis of β-lactoglobulin (β-LG), which is the major allergenic protein of bovine milk, holds significant importance due to its widespread occurrence and potential adverse effects on human health. Therefore, it is important to develop accurate, reliable, and highly sensitive methods for the analysis of β-LG. In this regard, 3D-printing, which is characterized by the possibility of creating layer-by-layer 3D-devices, offers a broad spectrum of possibilities in chemical analysis. Indeed, it allows the easy, precise, and low-cost development of customized devices for sample preparation, from a wide range of available materials that can be compatible with organic solvents. However, non-functionalized 3D-printed devices present certain drawbacks, such as low surface area and limited selectivity, precluding their widespread application in sample preparation. Among the available selective ligands that can be used for functionalizing 3D-printed devices, aptamers, which consist of single-stranded RNA or DNA oligonucleotides with less than 100 nucleotides, are an excellent alternative to prepare smart 3D-printed devices capable of selectively recognizing target molecules, including protein biomarkers.
In this study, a 3D-cylinder-shaped printed microextraction device was designed and the surface covalently modified with an aptamer for the in-vial selective extraction of the allergenic food protein β-LG prior analysis by capillary electrophoresis-mass spectrometry (CE-MS). The particularity of this device is that it was designed to fit inside the CE injection vials, allowing to perform the extraction, elution, and injection for CE-MS analysis with minimum sample handling. Different 3D-printed devices designs were tested to handle small sample volumes and obtain high surface areas for enhanced preconcentration factors of β-LG. The 3D-printed devices were subsequently functionalized with aptamers and characterized by scanning electron microscopy and by the amount of attached aptamer. The aptamer-functionalized devices were finally used to optimize and validate a method for the analysis of β-LG, which can be applied to the analysis of low levels of this allergenic protein in food matrices.

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Analysis of α-synuclein by on-line aptamer affinity solid-phase extraction direct mass spectrometry

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Keywords: *Aptamer, Capillary electrophoresis, Mass spectrometry, On-line solid-phase extraction, α-Synuclein*

We present an on-line aptamer affinity solid-phase extraction direct mass spectrometry (AA-SPE-MS) method for the rapid purification, preconcentration, and characterization of α-synuclein (α-syn), a protein biomarker with different post-translational modifications related to Parkinson's disease [Anal. Chim. Acta 1256 (2023) 341149]. The AA-SPE-MS method was developed taking as a starting point an on-line aptamer affinity solid-phase extraction capillary electrophoresis-mass spectrometry (AA-SPE-CE-MS) method described for the same protein biomarker in a previous work [Anal. Chem. 92 (2020) 1525–1533]. The adaptation required the fritless microcartridge and instrumental set-up used for AA-SPE-CE-MS, as well as substituting the separation voltage by a mobilization pressure of 100 mbar. Some other conditions and parameters, such as the sheath liquid composition and the drying gas temperature in the ESI-MS, needed also to be reoptimized.
Under the optimized conditions with recombinant α-syn standards, the method was repeatable in terms of migration times and peak areas, satisfactorily linear between 0.025 and 5 $\mu g \cdot mL^{-1}$, and the limit of detection was 0.02 $\mu g \cdot mL^{-1}$, leading to a sensitivity enhancement of 1000, 500, and 10 times compared to CE-MS, direct MS, and AA-SPE-CE-MS, respectively. The applicability of the developed AA-SPE-MS method was also evaluated for the analysis of α-syn from human blood after a simple thermo-enrichment clean-up pretreatment, pointing out the great potential of AA-SPE-MS for the rapid and sensitive targeted analysis of protein biomarkers in biological fluids.

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P-40

Determination of total petroleum hydrocarbons in water by solid-phase extraction (SPE) using shungite as sorbent: Green and efficient approach

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Keywords: *Total petroleum content, Solid-phase extraction, Shungite, Green method, Gas chromatography*

The determination of total petroleum hydrocarbons (TPH) in environmental samples is of paramount importance due to their potential adverse effects on ecosystems and human health. Solid-phase extraction (SPE) has emerged as a widely used technique for the extraction and preconcentration of TPH from various matrices. This study aims to explore the application of shungite, a carbon-based mineral with unique adsorption properties, as a sorbent material in SPE for TPH determination.

Oil is the most valuable raw material, without which modern civilization is impossible and hydrocarbon fuels account for 2/3 of world energy consumption. The existing demand for oil and oil products increases annually by an average of 8%, and production by 5.5%.

Oil pollution of the environment causes damage to the animal world and a direct threat to public health because of spills during the logistics transportation of oil products. This leads to the emergence of modern oil forensic research and analysis.

Improving methods for detecting pollutants in the environment remains an important challenge for the field of environmental analytical chemistry. The complexity of the analytical method in the accurate and correct detection of toxic chemical compounds in air, water, soil and bioenvironment in very low concentrations lies in the observance of high indicators of metrological characteristics (identification reliability, detection limit, selectivity, accuracy). Standard methods for the determination of petroleum products from soil, including extraction, purification from polar compounds, and concentration at the stage of sample preparation, require a laborious process. Standard methods for determining oil products in soil are very laborious at the stage of sample preparation and include extraction, purification from polar compounds, and concentration. Manual methods require organic solvents such as carbon tetrachloride, chloroform, hexane, and long analysis times (15 to 380 minutes). The consumption of solvents in volumes from 25 to 120 mL, concentration by evaporation, re-extraction (in the case of IR spectrometry) leads to the release of a large amount of toxic waste into the atmosphere.

One of the new methods is using shungite as a sorbent material in SPE cartridges or disks. Shungite's porous structure and high carbon content provide a large surface area for efficient adsorption of TPH compounds. The extraction parameters such as pH, extraction time, and elution solvent can be optimized to maximize the recovery and selectivity of TPH.

There are several green advantages of the utilization of shungite as a sorbent material in SPE. Firstly, shungite is a natural and abundant mineral, reducing the need for synthetic and potentially harmful sorbents. Secondly, shungite can be regenerated and reused, minimizing waste generation and lowering the overall cost of analysis. Additionally, the extraction process using shungite can be conducted under mild conditions, reducing the consumption of solvents and energy.

The efficiency and effectiveness of TPH determination using shungite-based SPE to be evaluated by analyzing environmental samples, including soil and water contaminated with petroleum hydrocarbons. The recovered TPH compounds also allows to quantify using appropriate analytical techniques, such as gas chromatography (GC) or infrared spectroscopy (IR). Compared with traditional sorbents selectivity and adsorption capacity of shungite much higher in its performance.

The proposed study aims to demonstrate the effectiveness of shungite as a sorbent material in SPE for TPH determination. This research has the potential to contribute to the development of green and efficient analytical methods for TPH analysis in environmental samples. The findings will provide valuable insights into the applicability of shungite in SPE and pave the way for its further exploration and optimization in environmental analysis.

P-41

Polymeric films modified with deep eutectic solvents for organophosphorus pesticides extraction from water samples

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Keywords: *Deep eutectic solvent, Functionalized membranes, Organic pollutant, Plasticizers, Thin-film microextraction*

The monitoring of different organic pollutant in waters is mandatory to control the levels of contamination in water bodies. Due to the lower environmental concentrations, a preconcentration step before the chromatographic analysis is required, using different types of sorbents. In this work, polymeric films modified with deep eutectic solvent (DES) [Sep. Purif. Technol. 239 (2020) 116486] have been prepared. The modified films are placed in contact with water samples following the principles of thin-film microextraction (TFME) [Anal. Chem. 75 (2003) 1002–1010], i.e. a piece of the film is suspended in the solution (several mL) for a predetermined time. The targets pollutants in this study are organophosphorus pesticides (OPPs): Ethoprophos, Parathion-methyl, Fenchlorphos, Chlorpyrifos, Protrophios and Azinphos-methyl.
The films are prepared by the solving casting method, with cellulose triacetate (CTA) as the polymer, and as a deep eutectic solvent, several mixtures have been evaluated containing dodecanoic acid, camphor or menthol, and lidocaine, at different ratios [ACS Sustain. Chem. Eng. 3 (2015) 2469–2477].
Preliminary results for the new films containing CTA/DES (70:30%) have been obtained. The extraction efficiency for OPPs using the films is quantitative for most of the studied compounds under 6 hours of extraction (20 mL solution fortified with 50 $\mu g \cdot L^{-1}$ of OPPs) in a rotary agitator. The ultrasound-assisted elution with ethyl acetate has provided good results. For the suspended configuration (S-TFME) using the DES (dodecanoic acid:lidocaine (2:1)):CTA film (70:30%), a calibration curve has been obtained placing a 2 cm^2 piece film immersed in the solution for one hour (S-TFME). Good correlation has been found in the working range from 1 to 130 $\mu g \cdot L^{-1}$. We have demonstrated that a polymeric film manufactured with DES ((dodecanoic acid:lidocaine (2:1)) and CTA can be used for the TFME of OPPs. Validation of the method and application to different water samples is still under investigation.

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Unleashing the potential of 3D-printing containing rare-earth metal-organic frameworks as fluorescence sensors for the determination of tetracyclines in seawater

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Keywords: *Metal-organic frameworks, 3D-printing, Front face fluorescence, Tetracyclines, Sensing*

3D-printing, a layer-by-layer methodology to create three-dimensional objects, has revolutionized the Analytical Chemistry field, thanks to its, recently numerous published applications. Moreover, this technology offers a wide range of possibilities, with techniques such as funded deposition modeling (FDM), stereolithography (SLA) and photopolymer inkjet printing (PIP), among others which provides specific devices with enhanced features. Specifically, SLA, in all its modalities, offers a series of advantages such as easy printing, high-printing precision, compatibility with organic solvents, simple surface modification, several available materials (transparent, elastic, etc.) and moderate cost. As a result, its use in all the fields has increased drastically in the last years. However, 3D-printed objects obtained through SLA modalities, in general, provides low surface areas and limited sensing characteristics. Therefore, it becomes necessary to combine the 3D-printed devices with other functional materials to obtain improved composites. In this regard, the incorporation of metal-organic frameworks (MOFs) is an intriguing opportunity to enhance the capabilities of the 3D-printed devices. Furthermore, MOFs can provide increased surface areas and concretely, the use of rare-earth MOFs can provide selective systems with fluorescence characteristics, thanks to quenching or antenna effects, for the determination of emerging pollutants. Hence, the combination of ad hoc 3D-printed devices and rare-earth MOFs can open new avenues in sensor development.
The aim of this work is to develop 3D-printed devices for front-face fluorescence and its surface modification with terbium-based MOFs for the detection of tetracyclines in seawater. For this purpose, tailored devices with specific angles were designed to be used in conventional benchtop fluorimeters. Afterwards, the impact zone of the excitation beam on the 3D-printed front face fluorescence device was modified with the terbium-based MOF. The different reaction steps and the presence of the MOF were confirmed through infrared spectroscopy and scanning electron microscopy. Next, the 3D-printed devices containing the terbium-based MOF were used to extract, preconcentrate and sense tetracyclines in water samples. The prepared composite at optimal conditions exhibited high-selectivity and low limits of detection, surpassing those obtained with terbium- and other rare-earth-based MOFs in dispersive mode. This improved feature was primarily attributed to the preconcentration capabilities of the composites. In conclusion, this study demonstrates the potential of 3D-printed-MOF composites as sensors for the analysis of emerging pollutants.

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Bisphenol A extraction using tailored 3D-printed stir-sticks modified with a selective aptamer

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Keywords: *Bisphenol A, 3D-printed devices, Aptamer, Surface modification, Extraction*

Bisphenol A (BPA) is a concerning emerging environmental contaminant due to its widespread presence, since it can leach from plastics into food and environment through multiple pathways. It is commonly used in the production of polycarbonate resins and serves as a stabilizer in various plastics. As an endocrine disruptor, it has the potential to disrupt mammary gland development, impact egg cells, and induce chromosomal abnormalities in humans. Moreover, it can alter the behaviour, reproductive success, and growth of aquatic organisms. Therefore, it is crucial to develop accurate analytical techniques to detect trace levels of BPA in the environment, identify sources and pathways of contamination, and establish strategies to mitigate its release and exposure.
In recent years, 3D-printing has emerged as an interesting alternative to conventional systems in the sample preparation field. This is owing to its advantages such as customized system preparation, cost-effectiveness, and easy fabrication. Among various 3D-printing methods, stereolithography offers exceptional features such as high resolution, superior surface quality, easy surface modification, and compatibility with organic solvents. However, the surface area and selectivity of 3D-printed devices is limited, and its combination with other functional materials to enhance their characteristics is necessary. In this context, aptamers, which are single-stranded nucleic acid molecules (DNA and RNA) with high affinity and specificity, are an interesting alternative to overcome the limitations of 3D-printing.
This study focuses on the development of a novel 3D-printed stir-stick design that incorporates surface modifications with an aptamer specific for BPA retention and subsequent determination. Extensive research has been carried out to ensure proper cleaning of the 3D-printed structure, characterize the surface modification with the aptamer and optimize the BPA extraction process. In addition, the extraction procedure has been applied to real environmental waters. The results showed the advantages of the ad hoc designed 3D-printed devices and the high selectivity achieved with the aptamer modification in the BPA extraction compared to other bisphenols and emerging pollutants.

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Use of paper-based devices modified with polyhedral oligomeric silsesquioxane-methacryl substituted monolith for the extraction of bisphenols from environmental samples

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Keywords: *Bisphenol, Paper-based devices, Extraction, Molecular imprinted polymer, Liquid Chromatography*

Bisphenol A (BPA) is an emerging contaminant that presents a big impact on the aquatic environment, since it is generally used in the synthesis of polycarbonate plastics and epoxy resins. However, it is being partially replaced in industrial applications by other compounds with similar structure such as bisphenol C or bisphenol S (BPC and BPS, respectively), among others. For this reason, these bisphenols (BPs) have been also detected as contaminants in environmental waters and also in aquatic organisms such as seafood or bivalves. It has been demonstrated that BPs are endocrine disruptors, which implies that continued exposure over time, even at low concentrations, can affect negatively aquatic life and human's health, altering reproduction and development and producing different diseases. For all the exposed above, it is necessary to control BPs presence in both environmental waters and aquatic organisms, consequently, the development of analytical methodologies able to simultaneously determine different types of BPs is highly desirable.

Paper has been present in Analytical Chemistry field for many years, but currently it has been rediscovered as a valuable device for analytes determination. In this sense, the use of paper-based sorptive phases has become a clear trend in the sample preparation context due to its benefits (low cost, easy modification, etc.)

In this work, a paper sorptive phase based on a polyhedral oligomeric silsesquioxane-methacryl substituted (POSS-MA) monolith have been developed and used as a low cost platform to extract BPs (concretely BPA, BPS, BPC, bisphenol AP and bisphenol AF), which were subsequently determined by HPLC coupled to both UV and fluorescence detection. Several extraction parameters such as loading and elution solvents as well as other variables (loading capacity and breakthrough volume) influencing on the analytical performance of the POSS-MA paper-based device were optimized. Under optimal conditions, the developed method was successfully applied to determine BPs present in environmental waters and foodstuffs. In all cases, satisfactory recovery values of BPs were obtained. Thus, the results demonstrated the suitability of the POSS-MA paper-based device to be used for effective extraction of BPs in different types of samples.

Acknowledgements

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P-45

Simultaneous determination of thymine, uracil and 5-fluorouracil in human plasma samples by hollow fiber liquid-phase microextractraction at-line coupled with capillary electrophoresis

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Keywords: *Automation, Hollow fiber liquid-phase microextraction, Capillary electrophoresis, Human plasma, Anticancer drug, Biomarkers*

The number of samples to be analysed in laboratories increases exponentially year by year due to technological advances but also to the great social concern to guarantee public health, environmental protection, and food safety. However, in most cases, direct determination of analytes in complex matrices, such as biological, environmental or food samples, is not possible, even when using highly sensitive analytical instruments. Thus, the high power and high sophistication of current analytical instruments contrast with the low speed and low degree of automation of sample treatment procedures. On the other hand, there is a steadily growing interest in monitoring high-complexity samples and in the determination of new endogenous and exogenous substances in minute sample volumes, which demands the development of novel miniaturised and automated analytical methods.
In this contribution, an at-line hollow fibre liquid-phase microextraction (HF-LPME) method coupled to capillary electrophoresis (CE) is presented for the determination and quantification of thymine and uracil at endogenous levels, and 5-fluorouracil at therapeutic levels in human plasma samples. 5-fluorouracil is an antineoplastic agent widely used alone or combined with chemotherapy regimens for treating several types of cancer (i.e., breast, ovarian, cervical, gastrointestinal, pancreatic, etc.) [J. Pharm. Biomed. Anal. 78–79 (2013) 129–135]. Nevertheless, response to treatment with this drug is highly variable and not always positive, and some patients may experience serious side effects at standard doses. These adverse effects are primarily related to a deficiency in dihydropyrimidine dehydrogenase (DPD), the enzyme responsible for the metabolism of more than 80% of administered 5-fluorouracil. It has been shown that subjects with DPD deficiency have significantly elevated concentrations of exogenous nucleobases in plasma and urine [J. Chrom. B 738 (2000) 249–258]. Hence, since fluoropyrimidines are catabolized by the same metabolic pathway as endogenous pyrimidines, the determination of endogenous pyrimidines in biological fluids may be useful as a predictive method before oncological therapies with 5-fluorouracil [J. Pharm. Biomed. Anal. 78–79 (2013) 129–135; Br. J. Cancer 116 (2017) 1415–1424].
In this contribution, we present a method for rapid, direct and simultaneous determination of thymine, uracil and 5-fluorouracil in human plasma samples. Sample treatment was carried out by in-vial extractions using a tailor-made set-up, based on the use of polypropylene hollow fibres (HF) as support for the liquid membrane (SLM) and designed for coupling the HF-LPME device directly to a commercial CE system [Talanta 238 (2022) 123068]. Dedicated 3D-printed vial inserts were used to ensure direct injection of the extract from the HF lumen. Target analytes were extracted from 50 µL of donor solution (with pH of approximately 7) into 5 µL of 100 mM NaOH as acceptor solution, using tributyl phosphate as the SLM immobilised in the pores of a 10 mm piece of an Accurel PP 300/1200 HF. The extraction time was 180 minutes, and no agitation was applied. Under these conditions, extraction recoveries were 48% for thymine, 30% for uracil, and 54% for 5-fluorouracil and the CE autosampler facilitated the simultaneous pretreatment and automated analysis of up to 42 samples. The proposed methodology was successfully applied to undiluted plasma samples with detection limits ranging from 2.7 $\mu g \cdot L^{-1}$ for thymine to 19.9 $\mu g \cdot L^{-1}$ for 5-fluorouracil. Automated couplings of HF-LPMEs to commercial CE instruments reduce the analyses times and costs, moreover, they incorporate new methodologies and advances that might significantly contribute to developing and implementing HF-LPME as a standard sample treatment method for a wide variety of complex matrices, including biological, as well as environmental and food samples.

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P-46

Development of two-steps extraction technique and LC-QTOF method for determination of cortisol and its metabolites in human plasma and animal faeces

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Keywords: *Cortisol, Stress, Noninvasive monitoring, High-resolution mass spectrometry, Solid-phase extraction*

Measuring steroid hormones is of huge importance for investigating stress levels in the fields of human activity and animal welfare. The glucocorticoids cortisol and cortisone are steroid hormones naturally synthesized in the adrenal cortex. Cortisol is transported in plasma bound to corticosteroid-binding globulin (CBG) and albumin. The concentration of cortisol and its metabolites in blood has proved to be useful indicator of stress [Steroids 75 (2010) 350–354]. Chronic stress and major depressive disorders are associated with cortisol metabolism which is characterized by a great number of structurally closely related metabolites. Blood collection from wild animals is difficult to perform and can be stressful for the animal. Therefore, in recent years the measurements of steroid hormones and its metabolites in feaces has gained increasing attention. The determination of faecal cortisol metabolites as a non-invasive method of monitoring stress is often used in hormonal studies in free-ranging animals [Ecol. Evol. 8 (2018) 9218]. Liquid chromatography-tandem mass spectrometry (LC–MS/MS) has a broad range of application across many different fields, including the clinical laboratory medicine for quantification of steroid hormones and their metabolites [J. Steroid Biochem. Mol. Biol. 129 (2012) 129-138]. The usefulness of LC-MS/MS methods for plasma cortisol and cortisone [J. Clin. Endocrinol. Metab. 104 (2019) 4827], salivary cortisol and cortisone [J. Clin. Transl. Endocrinol. 22 (2020) 100243] and synthetic glucocorticoids [J. Chromatogr. B 877 (2009) 765–772] have been described. In this study, we develop an analytical method for the determination of cortisol and its metabolites in human plasma and animal faeces using high-performance liquid chromatography connected to an accurate mass quadrupole time-of-flight 6550 iFunnel Q-TOF mass spectrometer equipped with Jet Stream Technology ion source. The development of the faecal method included an optimization of extraction and the purification steps to effectively separate target analytes. Optimization of chromatographic separation conditions and mass spectrometer parameters was performed for cortisol and its metabolites in extracts prepared from human plasma and faeces derived from European bison (*Bison bonasus*).

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An ecological, economical and efficient method for drug determination in blood samples

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Keywords: *Psychoactive substances, Blood, Solid-phase microextraction, White analytical chemistry*

According to European Drug Report 2021 [European Monitoring Centre for Drugs and Drug Addiction, European drug report 2021*: Trends and developments*] seizures of narcotic substances in the European Union have increased steadily over the last decade. Cocaine, MDMA and mephedrone remain among most popular drugs. In addition to the increased supply of certain substances, there are also concerns about the more and more frequent cases of acute poisoning, e.g. cocaine or MDMA.
For toxicological analyses, sample preparation for analysis is essential, due to the complex matrix. This step is often time-consuming and requires the consumption of large quantities of reagents. The method of microextraction to the solid-phase allows not only to reduce their quantity, but also to perform the analysis using small amounts of the sample, which is often available in limited quantities [Anal. Bioanal. Chem. 393 (2009) 781–795].
The purpose of the research was to develop a new method that would allow the determination of selected drugs (mephedrone, MDMA, and cocaine and its metabolites: benzoylecgonine, norcocaine, cocaethylene) in whole blood, while meeting not only the criteria of greenness, but also balancing ecological, analytical, and economic aspects. For this purpose, solid-phase microextraction was paired with capillary electrophoresis hyphenated to a mass spectrometer. The developed method was validated, and the determined parameters indicated its potential for routine toxicological testing. In addition to analytical parameters, its "greenness" and cost-effectiveness were also evaluated, thanks to the use of the WAC model developed by Nowak et al., [Trac–Trends Anal. Chem. 138 (2021) 116223]. The combination of SPME with CE-MS made it possible to reduce reagent consumption and thus also reduce the cost of analysis while maintaining analytical quality standards.

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P-48

Application of solid-phase extraction (SPE) with HPLC-DAD for analysis of the concentration of oxidative stress markers in urine of women with overweight after a 4-week energy-restricted ketogenic diet

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Keywords: *Ketogenic diet, Oxidative stress, Solid-phase extraction, Overweight*

Over the last few years, the prevalence of overweight and obesity is growing in the global population. Obesity results not only in the aesthetic problem but also can lead to serious health consequences. One of the factors contributing to the development of for instance cardiovascular diseases is chronic low-grade inflammation, closely related to oxidative stress. Reactive oxygen species generated during oxidative stress lead to cell dysfunctions, necrosis or apoptosis, as well as post-translational modifications altering signalling pathways. In individuals with obesity, the reduction of body weight is mandatory to decrease oxidative stress and low-grade inflammation. The ketogenic diet (KD) is an example of a diet which was found to be effective in reducing oxidative stress in animal models [Nutrients 14 (2022) 4805]. KD is a diet composed mainly of fat, with a limited intake of carbohydrates (<50 g per day) and leading to the ketosis state in the body. Although the interest in KD increased in the last years, still many effects of KD are not fully understood. For instance, the effect of KD on oxidative stress in clinical trials has not been confirmed. Therefore, the aim of this study was to evaluate the effect of 4-week energy-restricted KD on the oxidative stress markers in urine.
20 women with BMI >25.5 were randomly assigned to KD or standard diet for 4 weeks. Diets were equal in terms of calorie intake (1700 kcal) and were delivered daily to participants in the form of catering. KD contained 70, 30 and 20% of fat, protein and carbohydrate, respectively, while the standard diet contained 20, 30 and 50% of fat, protein and carbohydrate, respectively. Before and after the diet intervention, the anthropometric indices, blood samples and urine were collected. In urine samples, the concentration of two oxidative stress markers, namely 8-hydroxyguanosine (8-OHdG) and 8-isoprostane were analysed using previously optimized solid-phase extraction (SPE) method and HPLC with diode array detection (DAD).
The applied method has been found sufficient and effective to measure the oxidative stress markers in urine samples after nutritional interventions.

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P-49

Optimization of ionization process of steroid metabolites with the use of Design of Experiments approach

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Keywords: *Design of experiments, Mass spectrometry, Steroid hormones, Ionization, Optimization*

Effective quantitative determination of steroid metabolites (SM) can be a useful tool in the assessment of hormonal disorders accompanying the development of prostate cancer. Characteristic feature of SM is a compact, ring structure with different functional groups. Taking into account complicated nature of ionization process and difficulties in SM determination, optimization of ion source parameters for quantification of SM was necessary.
3 parameters, namely gas temperature, capillary voltage and nebulizer pressure were found to be crucial for ionization process of SM, based on preliminary research. To ensure the possibility of finding the optimal parameter settings, Design of Experiments approach was used. Based on the number of input parameters and the fact that curvature in the response surfaces might be expected, Box-Behnken Design (BBD) was chosen. BBD allows the evaluation of main effects, first order interactions and quadratic terms. Also, since BBD does not assume axial points, all experiments were performed within a predefined, safe, cubic design matrix. As a result, 15 experiments were planned (including 3 center point replications), with factors on 3 levels.
The applied parameter ranges were selected on the basis of literature data, as well as previously performed pilot study. In case of capillary voltage the value ranged from 2000 to 5000 V, gas temperature was tested between 180 and 350 ºC and nebulizer pressure was studied from 25 to 45 psi. Area under the peak, for each target analyte, served as response. 3 relatively high capillary voltages (2000, 3500 and 5000 V) were tested. The higher value of capillary voltage, the higher possibility for the ionization process. On the other hand, too high capillary voltage may cause reductive or oxidative processes. Additionally, it may lead to decreased intensity of signals caused by discharge effects. For this reason, this parameter is specific for each metabolite and should be optimized for each compound individually. Second parameter which may influence the ionization process is gas temperature. The higher temperature of drying gas, the faster the evaporation process. Consequently, the efficiency of ionization process is higher. In the proposed study 3 values of temperature 180, 165 and 350 °C were tested. Due to the high thermal stability of the analytes, it was possible to use relatively high values of this parameter. Similar influence on ionization process shows the pressure on the nebulizer. In the optimization process 25, 35 and 45 psi were evaluated.
Based on multivariate regression analysis 12 models, separate for each SM, were built. Such an approach enabled prediction of tested parameters influence on individual metabolite response. All models were statistically significant, with *p*-value ranging from <0.0001 to 0.0148 (R^2 ranged from 0.94 to 1). No statistical significance for the lack of fit tests confirmed adequacy of built models. The most significant variables in the built models were gas temperature and capillary voltage. Although nebulizer pressure (main effect, quadratic term or its interaction) was found statistically significant, this factor was found to be less important for ionization process of SM. Models built for individual metabolites, allowed to conclude that the majority of studied steroid compounds would benefit from different conditions. In some cases, *e.g.* for androsteron and dehydroandrosteron, preferred settings of gas temperature should be at opposite ends of the design space. Nevertheless, simultaneous optimization of all compounds was necessary, in order to find mutually favorable settings. With the use of maximize desirability function and assuming that all the discussed compounds are equally important (with the exception of estradiol) a compromise setting was achieved. Due to the fact that peak areas for estradiol in all experiments were relatively low, its importance for simultaneous optimization was doubled. The exact suggested parameters settings for positive ionization mode would be: gas temperature 314.7 °C, capillary voltage equaled to 3882.9 V and nebulizer pressure set at 44.7 psi. However, overall desirability values would hardly change in some small ranges for studied factors. For example, decrease in gas temperature from 314.6 to 300 °C (beneficial for estradiol) only reduces the fit by 0.42%. Two compounds determined in negative ionization mode have also been optimized in terms of ion source parameters. Due to the fact that drying gas temperature needs to be constant, its value for simultaneous optimization was locked. Using maximize desirability function optimal settings of nebulizer pressure and capillary voltage were indicated (3825.6 V and 45 psi).

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P-50

Mass spectrometry-based multiplatform method for untargeted metabolomic analysis of gastrointestinal stromal tumour

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Keywords: *Metabolomics, Gastrointestinal stromal tumour, Multiplatform, Treatment response, Mass spectrometry*

Metabolomics is a field of science than helps understand processes occurring in a living organism, and complements the knowledge about gene function or protein function. Applying metabolomics to study gastrointestinal stromal tumour (GIST) can bring answers to many questions regarding its development, treatment or diagnosis. GIST is one of the most common soft tissue sarcoma. Although novel therapies are developed, still GIST treatment is hindered by its various response depending on the underlying mutation. The aim of our project is to describe the GIST metabolome in different GIST subtypes as well as detect changes in metabolite levels under the influence of imatinib, which is a first-line treatment.
GIST samples were xenografts developed in mice from human tumours. Four xenograft models were used, which differed in the type of mutation in KIT gene. A total of 71 tumours were analysed, half of which were treated with imatinib. To cover the highest number of metabolites, we selected a method based on GC-MS and LC-MS with two types of stationary phases. Univariate (t test, ANOVA) as well as multivariate (partial least squares-discriminant analysis) stastistical methods were performed to compare the samples.
The applied analytical platforms enabled to measure a wide range of metabolites, from polar ones such as purines, amino acids, or carbohydrates to lipids such as fatty acids, phospholipids, or steroids. Based on the detected metabolites, samples group according to their mutational status, which seems to have the greatest influence on the GITS metabolome. Although the effect of treatment is less pronounced, it was also possible to indicate metabolites that were significantly affected by imatinib. As expected, drug-sensitive models yielded a higher number of statistically significant compounds than resistant tumours. We assume that purines and pyrimidines biosynthesis pathway may play a key role in mediating effective anti-cancer response. Nevertheless, more metabolomic studies are required to support the ongoing research on treatment effectiveness problems in GIST patients.

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Electromembrane microextraction (EME) of dialkyl phosphate metabolites in biological samples

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Keywords: *Dialkylphophates, Electromembrane extraction, Biological samples, Mass spectrometry*

Organophosphates (OPs) are a large group of chemical substances that have been widely used as pesticides in agriculture and household. Dialkyl phosphate metabolites (DAPs) are hydrolysis products of OPs that have been widely used as bioindicators to reflect exposure of OPs. Traditionally, OPs exposure has been associated with cardiovascular alterations, diabetes, Parkinson's and cancers. However, recent results demonstrated that OPs exposure disrupted thyroid endocrine function [Environ. Sci. Pollut. Res. 29 (2022) 79594–79604]. Animal studies have reported that OPs administration affects thyroid hormone levels, such as thyroid stimulating hormone (TSH), total triiodothyronine (tT3) or total thyroxine (tT4). Several studies have revealed that thyroid hormones are also affected by occupational exposure [Arch. Toxicol. 80 (2006) 449–457].
In this study, the simultaneously determination of 7 dialkyl phosphate metabolites (dimethyl, diethyl and dibutyl phosphates; dimethyl and diethyl thiophosphates; and dimethyl and diethyl dithiophosphates) was performed. The optimized method was compatible with mass spectrometry detection and was applied in biological samples to biomonitoring assessment of exposure achieving very sensitive levels of quantitation.
Sample treatment was performed by EME, a simple liquid-liquid microextraction technique based on the use of an electric potential to achieve a selective extraction across an organic solvent known as supported liquid membrane (SLM). Polypropylene hollow fibers were used as supported for the organic solvent. Analytes were extracted using a three-phase configuration with 1-octanol as supported liquid membrane.
The extracts were analyzed by ion pair liquid chromatography coupled to a triple quadrupole mass spectrometer (UPLC-TQ-XS, Waters™) using an Acquity UPLC® BEH C_{18} column (100 mm × 2.1 mm i.d., 1.7 µm particle size) at 40 ºC. Mobile phase consisted of a mixture H_2O (0.5 mM HCOOH/Tripropylamoniumformate) and acetonitrile at a flow rate of 0.4 mL/min for 12 min under gradient elution. The detection was performed with negative ionization in an electrospray source at 2.0 kV capillary voltage, 150 ºC for source temperature and 650 ºC for desolvation temperature. Under these conditions, the method allowed high sensitivity levels in the order of ng/mL. The proposed method was compared with other extraction methods, such as solid-phase extraction, liquid-liquid extraction with salting-out and QuEChERS previously reported methods.

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SPME analysis of *Lacticaseibacillus paracasei M12* and its prospects in the fight against *Erwinia amylovora*

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Keywords: *Solid-phase microextraction, Lacticaseibacillus paracasei M12, Erwinia amylovora, Antagonistic activity, Component composition*

This paper presents the results of the method of solid-phase microextraction combined with gas chromatography and mass spectrometry of screening microorganisms of the genus *Lactobacillus* isolated from natural sources against the causative agent of fire blight of fruit crops. 19 collection strains and 2 strains isolated from the phyllosphere of garden cenoses of Kazakhstan were analyzed. It was found that most of them had varying degrees of growth inhibition of the pathogen *Erwinia amylovora*. The zone of pathogen growth inhibition ranged from 25.0 ± 2.51 mm to 41.5 ± 1.5 mm. The highest inhibitory activity was in the bacterium *Lacticaseibacillus paracasei M12* (41.5 ± 1.5 mm). Somewhat lower in *Lactaseibacillus paracasei 33–4* (39.6 ± 6.65 mm) and *Lactobacillus plantarum 17M* (35.6 ± 0.57 mm). The characteristic of morphological, physiological, and molecular-genetic properties of the most active strain of *Lacticaseibacillus paracasei M12* is given. Chromatographic analysis of the culture liquid of the strain *Lacticaseibacillus paracasei M12* revealed antimicrobial metabolites produced by this bacterium. The test results revealed the presence of 29 volatile metabolites. The main active ingredient is lactic acid – 43.5%, acetic acid – 37.2%, butanoic acid – 1.2%, octanoic acid – 1.0%, benzoic acid – 1.4%, the content of 2,3-butanedione – 1.5%, 2,3-butanediol – 1.7% and acetoin – 12.4%. The centrifugation method was used for the accumulation of active substances with inhibitory activity in the culture fluid of the strain *Lacticaseibacillus paracasei M12*. As a result of the separation of the culture fluid into fractions (supernatant and biomass), it was found that the precipitated biomass had the maximum suppression zone. The dynamics of the accumulation of active substances in the culture fluid of the antagonist strain was determined and the optimal dosage of the biopesticide against the pathogen *Erwinia amylovora* was established. The bacterium strain *Lacticaseibacillus paracasei M12* can be used as a basis for a future biopesticide against fire blight.

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The forensic toxicology use of ion-pair reversed phase HPLC with UV detection in two fatal cases of sodium nitrite poisoning

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Keywords: *Reversed phase, Poisoning, Forensic, High-performance liquid chromatography*

Sodium nitrite is a globally known food additive, commonly used as a preservative against bacteria responsible for botulism. What is more, it is one of the components of antifreeze mixtures, corrosion inhibitor and it is a cyanide intoxication antidote. If consumed in larger quantities may result in life-threatening health situations. The goal of the research was to analyze two individual cases of intentional sodium nitrite poisoning in order to verify and study the presence of the toxin and its metabolites in the organisms. Both cases involve fatal intoxication in two men under the age of 40. They each acquired and ingested unknown amounts of a pure chemical substance which caused high methaemoglobinemia and thus inhibited the supply of oxygen to their tissues. Lethal dose of sodium nitrite is estimated to be 2.6 g, however, there are cases of non-lethal intoxications after much bigger dose administered.
Laboratory analysis of biological material collected during postmortem examination was conducted. For case 1 cardiac blood, gastric contents, liver, kidney and brain matter were collected, whereas in case 2 post mortem examination of the following materials had been harvested: blood (collected extravenously), vitreous humor, urine, cardiac blood, peripheral blood, bile, gastric contents, liver, kidney, and cerebellum.
The assay of both nitrate and nitrite levels was carried out with the use of ion-pair reversed phase HPLC with a direct nitrate and nitrite UV detection at low wavelength. The limit of detection for nitrite and nitrate assay was 200 ng/g. In both cases, the highest concentration of nitrite was detected in gastric content samples, as predicted.
What is more, bottled substances seized on the scenes of case 1 and 2, were delivered to the toxicology lab for confirmatory analysis. Both containers were labelled as sodium nitrite and the analysis confirmed that both substances found at the scenes contain nitrite of purity close to 100%.
Toxicological analysis confirmed the presence of nitrite in tested tissues acquired from both victims. Tissue nitrite levels have shown to be quite diverse between described cases of fatal nitrite ingestion, even in instances when approximately similar doses of the same substance have been ingested by the victims, making cases comparison problematic.

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Development of an aptasensor to determine Concanavalin A in food samples

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Keywords: *Sensing, Aptasensor, Concanavalin A, Graphene oxide, Fluorescence determination*

Concanavalin A (ConA) is a lectin found in legumes that is responsible for causing a typical allergy. This protein has strong affinity for α-D-mannosyl and α-D-glycosyl groups of glycoproteins and glycolipids. Structurally, ConA is composed of four identical subunits, forming a homotetramer, and each subunit is associated with a metal atom, typically manganese or calcium, which contributes to its binding affinity. Currently, there has been a significant increase in the use of aptasensors (APSs) for the detection and quantification of different analytes. APSs are based on aptamers, which are short, structured, single-stranded DNA or RNA molecules obtained by an in-vitro process called SELEX (*systematic evolution of ligands by exponential enrichment*). These aptamers are specifically designed to exhibit a high affinity for their target compound. In order to enable colorimetric or fluorimetric determinations, these aptamers can be modified by attaching a chromogenic or fluorogenic probe at one end of the DNA chain.

In this study, a fluorimetric assay in solution for ConA determination has been developed. For this purpose, ConA aptamer with an attached fluorescein probe was employed as APS. After the addition of graphene oxide (GO) to the aptasensor, a GO-APS complex was formed, leading to a quenching effect and a subsequent decrease in the initial fluorescence signal. However, after ConA addition into the solution, the equilibrium between GO and APS is disrupted due to the formation of a complex between ConA and APS. GO displacement results in a significant enhancement of fluorescence signal. This relative fluorescence increment is directly proportional to ConA concentration present in the sample. In order to optimize the assay's performance several experimental conditions such as APS and GO concentrations, as well as other parameters such as pH, temperature, and reaction time, were optimized. A limit of detection lower than 0.2 ppm of ConA (4 mg ConA/g sample) was obtained.

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P-55

Characterization of leaves, stem and roots of *Artemisia thuscula* for potential food and pharmaceutical applications

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Keywords: *Artemisia thuscula, Antioxidan activity, Flavonoids, Chlorophyll*

Artemisia thuscula is an endemic Canary Islands species of shrub characterized for its strong aroma, grey-silver leaves and yellow flowers. It is locally called as “incienso canario” and it has been traditionally used as diuretic, hypoglycaemic, antidiarrhoeic, uricosuric, stomachic spasmolytic, carminative, vermifuge, tranquillizer, pectoral, and anticatarrhal.
Plant flavonoids and pigments have strong antioxidant properties and have been associated with numerous health benefits. Moreover, incorporating plants with high content of water, minerals and fibre into diet contributes to maintain an adequate hydration, promotes digestive health, and helps regulate blood sugar and cholesterol levels. *Artemisia thuscula* plant material was collected at Barranquillo Frío (745 m, Santa María de Guía, Gran Canaria) in February 2023. The roots, stem, and leaves were separated, lyophilized and extracted with methanol for flavonoids determination. The antioxidant activity was determined with the radical 2,2-diphenyl-1-picrylhydrazyl assay. Pigments (chlorophyl a and b, and lycopene) were extracted with acetone and hexane from fresh leaves. Evaluation of water, mineral, and fibre content was carried out in leaves, stem, and roots.
The antioxidant activity of leaves, stem and roots were 74.84, 63.23 and 87.03% respectively. These parts of the plant exhibited higher antioxidant activity than the synthetic food additive BHT (32.66%), and the antioxidant activity of the roots was greater than the synthetic food additive BHA (78.85%). The same tendency was observed when total flavonoid content was evaluated, being the roots the part of the plant with the highest content of quercetin equivalents per gram of dry weight, followed by leaves and stem. The leaves presented 61.48% of water content and 8.69% of mineral content, while roots showed the highest fibre amount with 49.11%. Chlorophyl a was the prominent pigment, followed by chlorophyl b and lycopene.
The antioxidant activities of *Artemisia thuscula* as well as its flavonoids, chlorophyll and water contents, minerals and fibre composition make this plant a suitable option for food and pharmaceutical industry.

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P-56

Headspace sampling technique to enhance the volatile chromatographic fingerprint of foods

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Keywords: *Headspace extraction, Solid-phase microextraction, Multidimensional comprehensive gas chromatography, Food quality*

Volatile and semi-volatile compounds contribute to the distinctive aroma profile of foods and form a characteristic fingerprint that can be used to evaluate quality and authenticity of foods.
The most used sampling technique is by far solid-phase microextraction (SPME) that combines the easiness of operation with a high enrichment factor. Nevertheless, this technique requires often a trade-off between sensitivity and extraction time in order to maximize sample throughput.
This contribution presents different strategies that can be applied to enhance the sensitivity while shortening the extraction time, such as increasing the sorbent volume, sampling at reduced pressure, and performing multiple-cumulative trapping before the following GC×GC-MS analysis.
In particular, HiSorb, a commercial tool characterized by a coating volume roughly an order of magnitude greater than SPME, was used to characterize the volatile profile of brewed coffee, combined or not with multiple-cumulative trapping.
Vacuum-assisted SPME and multi-cumulative trapping SPME, as well as the combination of the two strategies, were applied to enhance the extraction, in particular of semi-volatiles from olive oil of different quality, i.e., extra-virgin, virgin and lampante olive oil. In combination with the enhanced separation obtained with GC×GC, it was possible to decrypt both the quality and geographical authenticity by the chemometric analysis of the information embedded in the volatile fingerprint.
All the three sampling strategies, alone or combined, and further coupled with GC×GC enhanced the overall level of information that can be extracted proving to be valuable tools for food analysis.

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P-57

Application of solid-phase microextraction for the analysis of aroma compounds generated during ripening of tomatoes fruits treated with synthetic immunity inducers

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Keywords: *Solid-phase microextraction, Aroma compounds, Two-dimensional gas chromatography, Immunity inducers, Tomato*

One of the preventive methods used to limit the losses caused by viruses is the application of synthetic immunity inducers, such as benzo(1,2,3)-thiadiazole-7-carbothioic acid S-methyl ester (BTH). In this project BTH has been used to affect the defense and developmental processes in tomato plants (*Solanum lycopersicum* L.) however the question arose if it would also affect the aroma of ripe tomato fruits. It is well known that aroma is one of the most important parameters in the quality check but also one of the main reasons for the consumers to accept and appreciate food products. Therefore this study aimed to compare aroma profile of ripe tomato fruits grown on the plants treated and without treatment with BTH.
The experiment was conducted on 3 varieties of tomato namely: Betalux, Money Maker and Alisa Craig, planted in soil. BTH was synthesized at the Poznań Science and Technology Park, AMU Foundation (Poland). It was used for watering seven- to eight-week-old plants (100 mL) in the concentration of 10 mg/L (control plants were water-treated). Ripe fruits were harvested, blended with 30% NaCl addition and subjected to analysis of volatiles. For the extraction of volatiles SPME 2 cm CAR/PDMS/DVB fiber has been used. Identification and semi-quantitation of key odorants was performed using multidimensional gas chromatography GCxGC equipped with two columns: SLB-5 (30 m x 0.25 mm x 0.25 µm) and SPB-50 (1.1 m x 0.25 mm x 0.25 µm) and time-of-flight mass spectrometer (TOF-MS). For semi-quantitation an internal standard has been used [2H8]naphthalene.
The results show that SPME is a useful technique to control quality of ripe tomatoes in terms of volatile profile. SPME-GCxGC/TOFMS allowed to identified (Z)-3-hexenal with green grassy odor note, hexanal with fresh grass odor note, 1-pentene-3-one with pungent odor and trans-4,5-epoxy-(E)-2-decenal with metallic odor. All of those compounds were reported as key odorants of fresh tomatoes therefore contribute to the their aroma. They are also known for their low odor thresholds ranging from 0.038 to 3.5 ug/kg of water.

P-58

In-solution trypsin digestion and LC-QTOF method for the identification of peptide markers differentiating meat species in processed food products

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Keywords: *In-solution digestion, Peptide markers, Liquid chromatography-quadrupole time-of-flight, Food authenticity*

Adulteration of meat products with meat of other animal species, offal, water, or cheaper proteins of animal or vegetable origin is a global problem reported worldwide [Food Chem. 342 (2021) 128240; Food Control 97 (2019) 15–24; Food Chem. 274 (2019) 857–864]. The increased production of processed meat products, their complex nature, and the variety of applied processing procedures as well as the increasing sophistication of adulteration pose difficulties in identification thereof and render the current detection methods still insufficient. Various analytical techniques are employed for identification of the species composition of food, e.g. electrophoresis [J. Food Sci. Technol. 55 (2018) 4984–4993], enzyme immunoassays (ELISA, Enzyme-Linked Immunosorbent Assay) [Lalahan Hay. Araşt. Enst. Derg. 58 (2018) 95–98], polymerase chain reaction (PCR) [Food Control 71 (2017) 346–352], and methods based on mass spectrometry (MS) [Trac–Trends Anal. Chem. 96 (2017) 99–106]. One of the latest, rapidly developing analytical methods is proteomics-based liquid chromatography-mass spectrometry (LC–MS), which has recently gained increasing acceptance in the food industry, for example, to identify protein-derived peptides that are resistant to thermal processing of food, making them useful for food authentication [Mass Spectrom. Rev. 40 (2021) 3–30]. In the present paper, we discuss the findings on the feasibility of using liquid chromatography coupled to high-resolution mass spectrometry (LC-HRMS) to identify unique peptides, i.e. the so-called authenticity markers enabling the differentiation of meat species in highly processed meat products. To identify peptide markers, samples of the most commonly consumed meat species were subjected to in-solution trypsin digestion. The tryptic protein digests were analysed using an Agilent Technology liquid chromatograph 1290 Infinity series connected to the quadrupole time-of-flight 6550 iFunnel Q-TOF MS equipped with a Jet Stream Technology ion source operated in the positive electrospray ionisation (ESI+) mode. Data processing and interpretation was performed using MassHunter BioConfirm and Spectrum Mill software (Agilent Technologies). The identified peptides were used to authenticate the meat species composition of highly processed food products. The undeclared presence of meat species was confirmed in 1 of the 10 samples analysed.

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Nicarbazin determination in glassy carbon electrode modified with multiwall carbon nanotube bucky paper

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Keywords: *Nicarbazin, Dinitrocarbanilide, Carbon nanotubes, Buckypaper electrode*

Nicarbazin is a type of anticoccidial drug, widely used to combat coccidiosis, a gastrointestinal parasite that affects the growth and development of the poultry industry in the world [Sci. Int. 1 (2013) 261–265; Food Res. Int. 99 (2017) 31–40]. Nicarbazin is a molecular complex of 4,4'-dinitrocarbanilide (DNC) and 2-hydroxy-4,6-dimethylpyrimidine (HDP) present in a 1:1 molar ratio [Poult. Sci. Rev. 5 (1994) 231-243]. HDP is rapidly excreted but DNC is retained in the tissues and can be found as a chemical residue in chicken meat. Due to this behaviour, the analysis of DNC in feed and chicken's meat is an important issue. The solubility of DNC in water is lower than 0.02 mg/L, which forces to use extraction methods before the analysis. Most of the analyses for the determination of DNC are widely carried out with liquid chromatography (LC), liquid chromatography coupled with mass spectrometry (LC-MS) and surface plasmon resonance (SPR), involving long time sample preparation, extraction procedures, high analysis cost and time consumption. In the European Union, the maximum amount of nicarbazin allowed in feed is 125 mg/kg [Food Res. Int. 99 (2017) 31–40]. The verification of the regulatory norm must be carried out quickly and in-situ, allowing decisions to be made such as discarding batches that do not comply with government regulations [Food Res. Int. 99 (2017) 31–40]. In this regard, electrochemical methods are shown as an alternative, low cost and easy to implement in-situ.

This work describes the results obtained by electrochemical analysis of DNC with new multiwall carbon nanotubes and polystyrene buckypaper electrodes (MWCNT/PS/BP). These electrodes are made of a large bucky paper and cut with a Silhouette Cameo 4 cutting machine to be easily adhered to glassy carbon electrodes or commercial screen printed electrodes, obtaining modified electrodes with a larger electro active area, and the ability to encapsulate compounds in the three-dimensional network formed by carbon nanotubes [Electrochim. Acta 443 (2023) 141984].

The DNC electro-reduction reaction was used as an analytical signal. DNC was electrochemically reduced from the nitro groups present in the molecule, the reaction occur via 4 electrons and 4 protons for each nitro group producing a hydroxylamine derivative. The measurements were carried out in a three-electrode cell in buffer Britton Robinson 0.1 M pH 5.0, using DNC (from Aldrich CAS 587-90-6) as standard compound. A calibration curve with a linear range between 4.53 and 75.56 mg/L was obtained using differential pulse voltammetry (DPV) as analytical technique. Limit of detection (LOD) and limit of quantification (LOQ) obtained were 4.36 and 14.54 mg/L, respectively. The results obtained were compared with those obtained in our laboratories using liquid chromatography. In summary, an easy to prepare electrode was obtained, low cost compared to the implementation of other techniques and capable of detecting DNC in the same detection ranges. It is a first advance for the development of a sensor for direct use in-situ for real samples.

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P-60

Determination of bisphenols and related compounds in honey and bee pollen samples

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Keywords: *Microplastics, Disruptive endocrine additives, Bee products, Microextraction, Liquid chromatography*

Nowadays, there is a great concern about the relationship between diet and its effects on physiological and pathological processes. Therefore, the demand for organic foods is increasing with special interest in which come from beehives as honey or bee pollen, due to their multiple healthy properties. Nevertheless, pollution by plastic products and microplastics (MPs) worldwide exposes pollinators as honeybees to multiple sources of pollution from different sectors. MPs are defined as plastic particles ranging in size from 5 mm to 1 µm, which are highly persistent and ubiquitous and may be transmitted through the trophic chain resulting in retention of environmental contaminants and release of additives causing even more toxic effects. Bisphenols and derivatives compounds are plastic components because they are used as chemical substances derived from plastics because they are used in combination with other chemicals to manufacture them. Moreover, bisphenols are classified as endocrine disrupting chemicals (EDCs) because they can act as xenoestrogens. These contaminants can be transported to the hive through foraging by bees and be transferred to the bee products, in addition to beekeeping practices or even the food containers used to their storage and distribution. Considering, the lack of regulation of these emerging contaminants as well as the associated risks, it is necessary to evaluate their presence in bee food products to guarantee the food safety of consumers and the pollinators too.
Therefore, the main objective of this study is to study the presence of hormone-disrupting compounds, mainly bisphenols, developing adequate analytical chromatographic methods by ultra-high performance liquid chromatography coupled to tandem mass spectrometry. Several stationary phases were tested to optimize the effects of various chromatographic parameters and detector-related parameters and several sample treatments were tested to optimize the extraction recovery and minimize the matrix effects for honey and bee samples, including traditional and miniaturized sample treatments. Finally, the proposed method was successfully validated and applied to quantify the target EDCs in honey and bee pollen.

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P-61

Two-step continuous SPE system with enhanced matrix removal sorbent combined with UHPLC-MS/MS for the determination of parabens and phenolic compounds in dairy products

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Keywords: *Phenolic compounds, Parabens, Dairy products, Solid-phase extraction, Ultra-performance liquid chromatography-tandem mass spectrometry*

Dairy products are an essential part in the western diet, being probably one of the most diverse groups of food products available in the supermarkets. It is well known that milk and dairy products can be contaminated by endocrine-disrupting chemicals (EDCs) from a huge variety of sources such as packaging, manufacturing processes, livestock contamination by environmental water and feed sources, etc. Parabens and phenolic compounds can reach the milk when cattle are directly exposed to environmental or feeding contamination [Food Chem. X 15 (2022) 100424].

For their analysis, it is observed that the most used techniques for parabens and phenolic compounds in dairy products are gas and liquid chromatography. Gas chromatography coupled to mass spectrometry is an effective choice for quantifying ECDs with good separation efficiency and a high throughput [Food Chem. Toxicol. 136 (2020) 110992]. On the other hand, high-performance liquid chromatograph coupled to mass spectrometry the other most used techniques. The main advantage of using liquid chromatography is that there is no needing of derivatizing the analytes, while in gas chromatography some of them will not be detected unless they are derivatized [Food Chem. Toxicol. 154 (2021) 112334].

In this work, a two-step continuous SPE extraction and purification method has been validated: first, the sample extract passes through an in line SPE sorbent combination, EMR-lipid and Oasis HLB-PRiME to cleaning-up the fats and lipids from the sample and then preconcentrate the analytes. The detection and quantification were carried out by UHPLC-MS/MS. This method allows the analysis of 28 EDCs with a huge increase of the recovery efficiency from 20 to 150% when a single SPE sorbent is used to 90 to 105% with the use of the proposed SPE combination. The method was validated for the determination of twenty-eight EDCs. The method was evaluated in terms of recovery (90–105%), matrix effects (0–10%), linearity, precision (relative standard deviation range, 3–12%), and limits of detection. Several samples were tested, making a total of 32 samples with different packaging materials (polystyrene, high-density polystyrene, multilayer cardboard, and polystyrene terephthalate). Bisphenol A and bisphenol Z where the most detected phenolic compounds, although they did not exceed the limit set by the European Regulations. From parabens, the highest concentration detected was for ethyl paraben in several dairy products.

P-62

Simultaneous determination of steroids and NSAIDs in milk and eggs collected from rural Roma communities in Transylvania, Romania based on DLLME-SFO and HPLC analysis

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Keywords: *Steroids, Non-steroidal anti-inflammatory drugs, Milk, Eggs, Dispersive liquid-liquid microextraction based on solidification of floating organic droplets*

The aim of this research is to determine the level of five steroids (hydrocortisone, estrone, estriol, 17β-estradiol and 17α-ethinyl estradiol) and four non-steroidal anti-inflammatory drugs (naproxen, ketoprofen, ibuprofen and diclofenac) in milk and eggs samples collected from the domestic and local market in 14 rural Roma communities in Transylvania, Romania.
Target compounds were extracted from milk and egg matrices by protein precipitation with 5% acetic acid in acetonitrile, followed by centrifugation, collection of the organic phase, and evaporation to dryness. For extract purification, the residue was dissolved in 10 mL of ultrapure water at pH 3, and the target compounds were extracted by dispersive liquid-liquid microextraction based on solidification of floating organic droplets (DLLME-SFO). The influence of the volumes of extractant (1-undecanol), dispersing solvent (acetonitrile), as well as the amount of salt was studied. The extraction procedure was optimized using a 2^3 experimental design. The JMP software and the desirability function were used for simultaneous optimization of the extraction conditions.
The target compounds were analyzed by high-performance liquid chromatography (HPLC) coupled with photodiode array detector (PDA). The developed extraction procedure ensures a good enrichment factor (130-145 for milk and 30-45 for eggs), a good extraction recovery (75-108.45% for milk and 72 to 118.73% for eggs except for hydrocortisone of which the extraction recovery was under 20%), and good sample clean-up. Good limits of detection (0.003 to 0.026 mg/L for milk and 0.006 to 0.105 mg/kg for eggs) and limit of quantification (0.010 to 0.079 mg/L for milk and 0.019 to 0.319 mg/kg for eggs) were obtained.
15 milk samples and 20 eggs were analyzed by the developed protocol. For milk samples, the steroid concentration ranges from 0.33 to 105.02 µg/L. The highest concentration was found for 17α-ethinyl estradiol, followed by 17β-estradiol, estriol, estrone and hydrocortisone. The concentration of NSAIDs varies between 0.41 and 83.82 µg/L, the order of amplitude being ibuprofen followed by naproxen, ketoprofen and diclofenac.
For egg samples, the steroid concentration varies between 0.5 and 3.6 µg/kg, with only estriol and 17β-estradiol being detected. The concentration of NSAIDs varies between 5.36 and 136.65 µg/kg, the most detected being ibuprofen followed by ketoprofen and naproxen. Diclofenac was not detected in any sample analyzed.

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P-63

A multi-step sample preparation coupled with gas chromatography-mass spectrometry for the quantification of rotundone in grapes

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Keywords: *Solvent extraction, Solid-phase extraction, Solid-phase microextraction, Sesquiterpen ketone*

The aromatic component is a fundamental parameter in the consumer's appreciation of wine since first impressions are often dictated by olfactory examination. Wine is one of the most complex agri-food products as it contains almost 900 compounds, of which only 10% are likely to contribute to the aroma. Among them, rotundone was first identified in 2008 as the aromatic compound responsible for peppery notes in red wines. It is often perceived positively by consumers. Rotundone is an extremely potent aroma, with olfactory detection thresholds of 8 ng/L in water and 16 ng/L in red wine. The growing number of research groups working on this topic around the world is evidence that rotundone is of great interest.
This work describes the development and validation of an analytical method for the quantitative determination of rotundone in grapes. The method uses stable isotope dilution analysis with *d5*-rotundone as internal standard, solvent extraction followed by solid-phase extraction and then direct immersion-solid-phase microextraction. The analysis is performed by gas chromatography–ion trap mass spectrometry. Fidelity, accuracy, linearity and limit of quantification were notably studied. The latter is in the range of 10-30 ng/kg of grapes. This method was applied to grapes of different varieties in order to evaluate the varietal capacity to produce rotundone. The concentration range obtained varies from <LOQ to 700 ng/kg.

P-64

A direct comparison of applying helium & hydrogen carrier gases with HS-SPME-GC-TOF-MS analysis of aroma active compounds in whisky

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Keywords: *Solid-phase microextraction, Hydrogen carrier gas, Aroma analysis, Green gas chromatography, Hydrogenation artefacts*

The use of solid-phase microextraction (SPME) hyphenated to gas chromatography and mass spectrometry (GC-MS), for the analysis of aroma active volatiles is widely accepted and applied as an effective technique to provide insights during characterisation, quality screening and process development of food and beverage raw materials and products.
Additionally, SPME is a relatively green analytical approach due to considerable reduction in solvent volumes, the amounts of sample and extraction time required.
With growing emphasis on green analytical approaches, increased analysis throughputs and reducing costs, there is significant interest in using hydrogen carrier gas instead of helium for GC-MS workflows. Helium costs have been increasing year on year in the last decade, whereas hydrogen can be safely supplied on-demand, via generators and allows superior gas chromatographic performance, enabling increased analysis speeds whilst maintaining or improving separation efficiency.
However, unlike helium, hydrogen is a reactive gas and the possibility exists for the formation of artifacts within the analytical system. Previously, a comparison of helium and hydrogen carrier gas, being used in conjunction with various SPME fibres, reported hydrogenation of unsaturated species to varying extents, when using hydrogen, depending on the fibre phase type and desorption conditions used [Phytochem. Anal. 33 (2022) 386–391].
In this study, we analysed the same whisky sample using helium and hydrogen, together with a range of SPME fibre phase chemistries and desorption conditions. A number of aroma-active compounds with varying degrees of unsaturation were chosen to investigate the occurrence and extent of hydrogenation between conditions. Additionally, the relative detection intensities and analysis precision of these compounds as well as other important aroma compounds were compared.
Here we report the degree of hydrogenation observed when using hydrogen and mixed-bed SPME fibre phases (i.e., CAR/DVB/PDMS), compared with 100% PDMS phases. Differences in extraction selectivity for some key aroma active compounds when using different SPME phases are also presented.

P-65

Aroma profiling of coffee varieties and blends to investigate quality and authenticity via automated high-capacity sorptive extraction (HiSorb) with GC–MS

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Keywords: *Food science, Authenticity, High-capacity sorptive extraction, Cryogen-free thermal desorption, Automated chemometrics*

Coffee is one of the most popular beverages globally due to its characteristic flavour and stimulative properties. Global scale production compiles beans from around 60 countries, with approximately 98 million cups consumed daily just in the UK. The coffee brewing process can affect perceived flavour and aroma, while coffee bean variety and geographical origin are also significant areas of consumer preference. There are two main varieties of bean and customers are more likely to pay 20-25% more for Arabica, a more expensive coffee, compared to Robusta. This can lead to fraudulent blends and even some farmers taking the risk of selling inferior quality coffee as higher quality for an increased sale price.

Determining quality and authenticity can be challenging due to the highly complex mixture of volatile organic compounds (VOCs) that provide coffee with its distinct flavour and aroma. These organoleptic compounds may also be present at very low levels and so, sensitive analysis is essential to ensure trace, yet important and potentially unique, components can be detected.

Here, samples were extracted using automated high-capacity sorptive extraction (HiSorb) on the Centri platform. HiSorb probes contain a larger phase volume than traditional SPME fibers, allowing more of each analyte to be extracted from a sample. After sampling the probes are automatically desorbed and analytes are further preconcentrated on a cryogen-free focusing trap. This powerful combination allows an enhancement in sensitivity to be achieved for subsequent GC–MS analysis. Finally, ChromCompare+, an easy-to-use data analysis and chemometrics platform, was employed to identify subtle differences between the coffee bean profiles.

In this poster, we demonstrate a fully automated workflow to investigate aroma profiles for coffee varieties and determine key VOCs that have the potential to be used for authenticity and quality purposes.

P-66

Hydrophobic natural deep eutectic solvents based on L-menthol as supported liquid membrane for hollow fiber liquid-phase microextraction of triazines from environmental water samples

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Keywords: *Hydrophobic natural deep eutectic solvent, Hollow fiber liquid-phase microextraction, L-menthol, Triazine herbicides, Aqueous samples*

This work proposes the use of a hydrophobic natural deep eutectic solvent (NADES) as a supported liquid membrane (SLM) for hollow fiber liquid-phase microextraction (HF-LPME) of triazines. NADESs were prepared using L-menthol as hydrogen bond acceptor combined with different hydrogen bond donors of natural origin: organic acids, alcohols and amines. Studies were carried out to determine whether the prepared NADESs met the necessary requirements to be used as SLM such as stability in the HF and compatibility with HPLC. Then, the ability of each prepared NADES to extract 6 triazine herbicides by HF-LPME from aqueous samples was evaluated. Among them, the mixture L-menthol:formic acid (1:2) provided better extraction results and was selected as SLM. Factors influencing the extraction efficiency of the proposed method, including pH of the sample and acceptor solution, salt content of the sample solution, extraction time and agitation rate, were carefully studied and optimized. The optimized HF-LPME procedure was applied to the analysis of water samples such as artificial water containing humic acids, river and spring water samples, with excellent clean-up ability for all samples analyzed. Additionally, the use of the selected NADES in the HF-LPME technique provided a more environmentally friendly approach.

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P-67

Synthesis and evaluation natural deep eutectic solvents (NADES) in the development of a sustainable extraction method of triazines in agricultural soils

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Keywords: *Natural deep eutectic solvents, Ultrasonic-assisted extraction, Triazines, Agricultural soils*

In the last decade, natural deep eutectic solvents (NADESs or natural DESs) have gained much attention as a viable and sustainable alternative to traditional organic solvents in multiple areas of analytical chemistry, including extraction techniques for contaminants in samples of environmental concern. Advantages of NADESs over traditional solvents include low volatility, being liquid at room temperature, biodegradability, low toxicity, and ability to dissolve complex substances. In addition, NADES preparation is easy and low-cost, consisting just in a two component mixture of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) substances of natural origin.
In this work, an environmental friendly ultrasonic-assisted extraction method for triazinic herbicides in soil samples have been developed using NADESs as extracting solvents and HPLC-UV (220 nm) for final determination of selected triazines. Choline chloride (ChCl) was used as HBA in the present work, and different organic acids, alcohols and amines were tested as HBDs in different molar ratios in order to find an optimum combination to form appropriated NADES for the extraction triazines. Among the different ChCl:organic acids mixtures tested, those consisting of ChCl:formic acid and ChCl:acetic acid, both in ratio 1:2, presented the better chemical properties (pH, water miscibility, stability at room temperature, etc.). Concerning amines, no NADES could be obtained with any of the combination assayed, and among the alcohols tested, 2,3-butanediol and 1,3-butanediol were found to be the most appropriated for NADES formation. A multifactorial design was then used to further evaluate these optimum NADESs for the ultrasonic-assisted extraction of triazines in soil at different times and temperatures.

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Preliminary evaluation of natural deep eutectic solvents for the ultrasound-assisted extraction of sulfonamides from soil samples

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Keywords: *Natural deep eutectic solvent, Ultrasound-assisted extraction, Sulfonamides, Soil*

Natural deep eutectic solvents (NADESs) are a class of novel solvents based on a mixture of components that act as hydrogen bond donors (HBD) and acceptors (HBA). These solvents are considered to be green, sustainable, cheap, and non-toxic, thus overcoming the toxicity of organic solvents. They are used in various scientific and industrial fields, such as the extraction of natural products for pharmaceutical applications. In the present study, different NADESs, based on choline chloride as HBA and carboxylic acids as HBD, were evaluated as solvents in the extraction of sulfonamides in soil. Sulfonamides are a synthetic class of antimicrobial compounds that can enter into the soil environment through the excretion of faeces and urine from grazing animals, the recycled water, or the application of sewage sludge, bio-solids and manure as soil amendments and fertilizers. The extraction of sulfonamides was carried out with different NADESs using ultrasound-assisted extraction (UAE) followed by dispersive solid-phase extraction clean-up and liquid chromatography tandem mass spectrometry detection using electrospray as the ionization source. Variables such as temperature and sonication time, type of clean-up adsorbent and soil moisture were evaluated, for each NADES used as solvent, in the extraction efficiency of sulfonamides from soil.

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A liquid microextraction based one-step method for the chemical fractionation of copper in seawater

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Keywords: *Copper fractionation, Seawater, Metals, Three-phase microextraction solvent bar, Graphite furnace atomic absorption spectroscopy*

The study of trace metals in seawater often requires a sample preparation step prior to their instrumental determination. In most of cases, either liquid-liquid extraction or solid-phase extraction are used with this purpose. However, in recent decades, a big effort has been made towards the development of greener and more efficient procedures for sample preparation in the analysis of trace metals. In particular, the use of liquid-phase micro-extraction (LPME) has become widespread, and several methods can be found for the separation and pre-concentration of trace metals, including single drop microextraction (SDME), dispersive liquid-liquid microextraction (DLLME), and hollow fiber liquid-phase microextraction (HF-LPME).
The three-phase microextraction solvent bar is a technique used in analytical chemistry for the extraction and preconcentration of analytes from complex samples. It is particularly useful for the analysis of trace elements and organic compounds in various matrices, such as water, soil, and biological samples. In this technique, a small volume of an organic solvent is immobilized within a porous material that can extract the analytes, such as a porous fiber or a membrane. The solvent bar is then placed in contact with the sample, creating three phases: the sample matrix, the organic solvent, and the porous material. Due to the high surface area and the nature of the solvent, analytes partition between the sample matrix and the sorbent modified with the solvent is achieved, effectively extracting them from the sample.
The three-phase microextraction solvent bar offers several advantages. Firstly, it allows for the extraction of a wide range of analytes with different polarities. Secondly, it provides high extraction efficiency and selectivity, resulting in improved detection limits. Additionally, the technique is relatively simple, cost-effective, and environmentally friendly compared to traditional extraction methods.
After the extraction process, the analytes are typically quantified using analytical techniques such as graphite furnace atomic absorption spectrometry (GFAAS). This technique is widely used for the determination of trace elements in various samples. It is based on the principle of atomic absorption spectroscopy, where the analyte atoms absorb light at a specific wavelength corresponding to their electronic transitions.
In GFAAS, the sample is introduced into a graphite furnace where it undergoes thermal decomposition, atomization, and vaporization. A beam of light at the characteristic absorption wavelength of the analyte is then passed through the atomized sample, and the amount of light absorbed is measured. The absorption signal is proportional to the concentration of the analyte in the sample, allowing for quantitative analysis.
GFAAS offers excellent sensitivity, selectivity, and accuracy for the determination of trace elements. It is widely used in environmental analysis, pharmaceutical research, food testing, and many other fields where the quantification of trace elements is essential.
In this work, we present an approach for the selective separation of inorganic and organic copper fractions in seawater using the Cyanex® 272 reagent in a three-phase microextraction solvent bar system. Optimized conditions for microextraction of Cu fractions resulted in an enrichment factor of 51.6 ± 2.3. Experimental results were in good agreement with theoretical data for Cu speciation, and the relationship between the enrichment factor and the concentration of dissolved organic carbon (DOC) in the samples was used to predict the total Cu concentration. The instrumental determination of Cu exhibited a linear response in the range of 0.1 to 20 $\mu g \cdot L^{-1}$, with a detection limit of 0.03 $\mu g \cdot L^{-1}$. We applied our method to the analysis of Cu fractions in seawater samples collected from the Bay of Cádiz (Spain). Our approach provides a promising tool for selective extraction and detection of copper in seawater, which could have implications for environmental monitoring and management.

P-70

Multivariate aluminium metal-organic frameworks as adsorption materials in analytical microextraction

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Keywords: *Metal-organic frameworks, Adsorption, Organic pollutants, High-performance liquid chromatography, Environmental analysis*

Metal-organic frameworks (MOFs) are crystalline coordination polymers composed by a metal center (or metal cluster) coordinated by organic ligands. The geometry and structure of the crystal lattice vary depending on the selection of these secondary units. Thus, the metal centers dictate the coordination while the organic ligands determine the number of connected centers. There is a long list of properties that make MOFs materials of great interest. Among them, their highest surface areas reported, their high thermal and chemical stability, and their versatility, are worth of mention. In addition, the MOF design process allows the creation of a wide variety of different materials, which are primarily the result of combining different metals and ligands. This heterogeneity does not end there. In fact, since 2010, more complex compounds called multivariate MOFs (MTV-MOFs) have been described. MTV-MOFs are formed by a metal center combined with two or more types of ligands. These materials allow for greater spatial structural diversity, as well as some heterogeneity, without altering the topology of the crystal. These changes seek a higher degree of functionality in the characteristics of the material, even improving the properties of the original structure.

The use of MOFs and their composites as sorbents in a variety of microextraction techniques is a widely used strategy nowadays for sample preparation. Thus, MOFs have been used for the extraction of analytes with interesting properties or with potential harmful effect on society (e.g. drugs, pollutants, etc.) from environmental, biological, and food matrices samples.

In this study, MTV-MOFs consisting of Al(III) have been prepared using two different ligands, fumarate and mesaconate, which produce the well-known MIL-53(Al)-FA and CIM-80(Al) MOFs, respectively. The former has the structure of MIL-53 with rectangular pores and it may exhibit a breathing phenomenon, while CIM-80(Al) has the MIL-68 structure with triangular and hexagonal pores. The objective of this work is the preparation of MTV-MOFs with different mesaconate:fumarate rates, and the evaluation of the ligand influence on the crystalline structure and the adsorption properties of the resulting MOF. The resulting materials were properly characterized, and the adsorption kinetics of the MOFs towards the extraction of different organic pollutants from water are also evaluated, thus gaining insights about the performance of this type of MOFs for their use in sample preparation.

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Automated determination of iodate using the iodine-starch reaction: A Lab-In-Syringe method

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Keywords: *Iodate determination, Iodized salt, Lab-in-syringe automation technique, Iodine-starch reaction*

This work describes a simple, green, and sensitive method automated by Lab-In-Syringe (LIS) for the determination of iodate. The set-up LIS system was applied to the quantification of iodate in table salts. As green and economic yet nonetheless selective alternative to the catalytic Sandell-Kolthoff reaction based on cerium and arsenite, the iodine-starch reaction was used and fine-tuned regarding sensitivity and linearity of response. Herein, triiodide is generated in acidic medium in the presence of an excess iodide that forms a steel-blue colored complex by being imbedded in the amylose helix that is measured online by spectrophotometry [Talanta 63 (2004) 339–343]. For this reaction, step-by-step addition of reductant, acid, and soluble starch to the sample is required, to which LIS presents an ideal automation tool. In this technique, the void of a glass syringe mounted on an automatic syringe pump serves as mixing and reaction chamber. Homogeneous solution mixing is enabled by the use of a magnetic stirring bar placed inside the syringe and driven by generating a rotating external magnetic field [Molecules 25 (2020) 1612]. Optimization of the essential experimental parameters (reaction time, reagent concentrations and volumes, aspiration order, and system cleaning) is described. The optimization achieved a considerable improvement in terms of response linearity and method sensitivity. This enabled the employment of the triiodide-starch assay for the determination of iodate down to concentrations of 2.0 µmol/L (LOQ) with a sample throughout of 3 h^{-1}. Above all, the presented method is characterized by high reproducibility (1.8%), simplicity, and greenness, that was evaluated following the AGREE metric tool as 0.7 [Anal. Chem. 92 (2020) 10076–10082].

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P-72

Comparison of two novel ionic liquids modified-monoliths in spin columns for the extraction of β-blockers from urine

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Keywords: *Glycidyl methacrylate-based monoliths, Spin columns, β-Blockers, Preparation approaches, Incorporation of ionic liquids*

Two novel approaches to isolate β-blockers in human urine were developed to incorporate an ionic liquid (IL) into a polymeric glycidyl methacrylate (GMA)-based monolithic matrix in spin columns. Prior to in-situ UV polymerization, and with the purpose of achieving covalent binding of monolithic beds to wall support, the inner surface of polypropylene centrifugal devices was treated with benzophenone and ethylene glycol dimethacrylate. The incorporation of ILs was performed following two different routes: (i) in-situ generation of IL onto the surface of the GMA-based monolith, and (ii) copolymerization by addition of the IL to the polymerization mixture. Specifically, the first route consisted in the functionalization of the GMA parent monolith with 1-methylimidazole (MIM) to generate the IL onto the monolith, according to a protocol based on previous articles by Herrero-Martínez et al. For this purpose, a 25% (w/w) MIM solution in acetonitrile was passed through the bare polymer at 75 °C during 8 h. The resulting material was washed with methanol. The second route consisted in the introduction of the IL 1-allyl-3-methylimidazolium chloride ([AMIM][Cl]) in the polymerization mixture. The first approach was unsuccessful due to the sorbent fragility after IL incorporation. In contrast, the second approach offered appropriate mechanical resistance and good flow-through properties. Composites containing 24 wt% [AMIM][Cl] provided the largest retention of the target compounds. Compared with other published methods for sample preparation of β-blockers, the solid-phase extraction (SPE) devices showed less environmental impact, a low cost and easy synthesis of the sorbent material, which can be >20 times reused after a simple regeneration step. The format of the polymeric monolith in spin column is highly competitive for multiple sample processing, and can be extended to routine bioanalytical applications.

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P-73

Development of galactose-functionalized methacrylate polymeric materials for selective extraction of food allergen lectins

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Keywords: *Food allergen protein, Galactose-based affinity sorbent, Phytohemagglutinin, Solid-phase extraction*

Lectins are glycoproteins, present in some parts of the plants, which selectively recognize and reversibly bind to carbohydrates and glycoconjugates through their binding sites. In the last years, and due to the increasing interest in food allergy field, most of the studies related to lectins are focused on the relation between the ingestion of lectin-containing foods with several allergic responses. Protein isolation and purification of these glycoproteins are essential steps in protein analysis schemes and proteomic techniques. However, the available commercial phases for lectins show certain flaws such as their limited mechanical stability, the lack of precise information about the amount of immobilized ligand, and consequently, their binding capability. Consequently, the development of novel sorbents with satisfactory extraction efficiency and selectivity for these protein species is highly desirable.
In this study, glycidyl methacrylate (GMA)-based materials functionalized with different galactose derivatives were prepared as affinity SPE sorbents for the analysis of several food allergen lectins (such as phytohemagglutinin (PHA)). For this purpose, GMA-based polymers were synthesized and subsequently functionalized with galactose derivatives using two different synthetic routes. In the first approach, the bare polymer was modified with ethylenediamine and glutaraldehyde, being two galactose derivatives next immobilized. In the second strategy, the starting polymer was modified with cystamine and gold nanoparticles (AuNPs), on which a thiolated galactose derivative was subsequently attached. The resulting materials were morphologically characterized by scanning electron microscopy and used as SPE sorbents for the isolation of PHA (as a case of study) from foods. Different extraction parameters (sample pH, eluent solution composition, binding capacity, sample volume, selectivity, and reusability) were evaluated. The material that provided the best PHA extraction performance was successfully applied to the selective extraction of PHA as well as other similar lectins from different foods (such as red and lima dried beans, fresh soybeans, and biscuits containing soybean protein traces as indicated in their label). After SDS-PAGE of the eluted fractions, all samples only exhibited the characteristic PHA band around 30 kDa, suggesting the high potential of the developed material for application in food allergy field.

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Development of an aptamer-based stir bar sorptive extraction for the determination of β-lactoglobulin in food using MALDI-TOF-MS

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Keywords: *Allergenic milk protein, Aptamer, β-Lactoglobulin, Stir bar sorptive extraction, Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry*

Bovine milk and dairy products are the most common foods causing allergies in infants, being β-lactoglobulin (β-LG) the most abundant allergenic protein. Thus, to prevent the incidence of allergic diseases and ensure the consumers' safety, it is mandatory to develop accurate and sensitive detection and quantification methods for β-LG determination. These methods often require an adequate sample treatment to remove interferents while the targeted analytes are preconcentrated. In this sense, stir bar sorptive extraction (SBSE) has opened new possibilities for sample preparation since it offers multiple advantages; however, it has been scarcely applied to proteins due to the lack of selectivity of most of the available commercial coatings. To improve the selectivity of SBSE coatings, the use of aptamers could be a potential alternative due to its high specificity against the target analyte.

In this work, a novel aptamer-functionalized SBSE coating was developed for selective isolation, preconcentration and determination of the allergenic milk protein β-LG, followed by a rapid, simple, and accurate identification and determination by matrix-assisted laser desorption/ionization mass spectrometry (MALDI-TOF-MS). For this purpose, the polytetrafluoroethylene surface of commercial magnetic stirs bars was properly modified and vinylized to immobilize a thiol-modified aptamer against β-LG via straightforward "thiol-ene" click chemistry. The aptamer-functionalized stir bar was employed as SBSE sorbent to isolate β-LG, and several parameters that can affect the extraction efficiency were optimized. The aptamer-based SBSE pretreatment with MALDI-TOF-MS provided suitable linearity (0.25–50 $\mu g \cdot mL^{-1}$) and a satisfactory limit of detection (0.08 $\mu g \cdot mL^{-1}$). The applicability of the method for the determination of low levels of β-LG was shown by analyzing milk-free foods (i.e., a 100% cocoa dark chocolate, a hypoallergenic formula for infants, and a dairy-free white bread) and milk-containing white breads. Recoveries ranged from 84 to 93% and repeatability in terms of relative standard deviation (RSD) was less than 2.2%. Also, outstanding advantages for the developed aptamer-functionalized stir bar coating include convenient and simple preparation and operation as well as satisfactory reusability.

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Introducing an environmentally friendly method for detecting aflatoxins in pistachios: An innovative approach utilizing deep eutectic solvents

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Keywords: *Aflatoxins, Deep eutetic solvents, Pistachio, Liquid chromatography*

Since their discovery in the 1960s, aflatoxins have presented a significant public health concern and posed a difficult challenge for ensuring food quality control. The fact that these carcinogenic substances are found in various food sources like nuts, maize, rice, and dairy products has prompted authorities to establish maximum allowable levels for these contaminants in these specific goods. Given the moderately polar nature of these compounds, official methods rely on employing methanol/water or acetonitrile/water solutions as extraction solvents. Moreover, since the contamination levels can vary within a batch, a considerable amount of both the sample and the extraction solvent is needed for analysis, resulting in a substantial amount of waste generated during the process. Additionally, samples of pistachios, complex and rich in lipids and other interfering compounds, require a crucial sample preparation step before analysis. A novel technique utilizing deep eutectic solvents (DESs) as extraction solvents is proposed to address these challenges. DES belongs to a new category of environmentally friendly solvents that combine a hydrogen bonding donor and acceptor in the right molar ratio, resulting in a clear solution with a significantly lower melting point than its constituents. Most DESs have demonstrated non-toxic and biodegradable properties and excellent extraction capabilities for various target compounds. Given the complex nature of the extract obtained from aflatoxin-contaminated pistachios, an additional purification and concentration step was necessary. The DES extracts were diluted with water and passed through a C_{18} solid-phase extraction (SPE) cartridge, where the trapped aflatoxins were subsequently eluted using a minimal amount of methanol and analyzed by ultra-high performance liquid chromatography coupled with a fluorometric detector, using a 2-µm partially porous C_{18} column. The mobile phase consisted of a linear gradient elution system using methanol and water, ranging from 30 to 60% MeOH over a period of 7.5 minutes. The flow rate was set at 0.45 mL/min, the injection volume at 2 µL, and the column temperature maintained at 35 °C. This approach demonstrated the viability of using DESs as extraction solvents for such a complex sample matrix, thereby reducing the reliance on organic solvents and minimizing process waste.

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Determination of polyaromatic hydrocarbons in wastewater using triazole functionalized silica sorbent based stir bar-supported micro-solid-phase extraction coupled with gas chromatography mass spectrometry

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Keywords: *Micro-solid-phase extraction, Polyaromatic hydrocarbons, Gas chromatography, Mass spectrometry*

Polyaromatic hydrocarbons (PAHs) are one of the major classes of widely distributed potent human carcinogens that are present in the environment through partial combustion of organic matter. In this work, N-sulfonyl-4-(phenanthren-9-yl)-1,2,3-triazole functionalized silica sorbent was employed as effective sorbent for the extraction of eight selected PAHs in water. The N-sulfonyl-4-(phenanthren-9-yl)-1,2,3-triazole functionalized silica sorbent was synthesized via two steps: first, the azide functionalization of silica and second, its click reaction with 9-ethynyl phenanthrene. The formed sorbent with high electron density and aromaticity was characterized using Fourier transform infrared spectroscopy, scanning electron microscopy and elemental analyzer. The large delocalized π-electron system in the sorbent will attract PAHs via π–π stacking interactions. Thus, the sorbent was used in a stir bar-supported micro-solid-phase extraction (SB–μ–SPE) of the eight selected PAHs in 10 mL water samples, and in combination with gas chromatography–mass spectrometry (GC–MS). Extraction optimization was achieved with sorbent mass of 5 mg, dichloromethane desorption solvent, 300 μL desorption volume, 10 min extraction time, 10 min desorption time and ionic strength of 2.0 g NaCl. PAHs analytes calibration gave desired linearity range with R^2 value of up to 0.9923 and detection limit of between 0.25 to 0.38 ng·mL^{-1}. Relative standard deviation (RSD) and relative recovery experiments were tested using PAHs spiked at 2.5, 5 and 10 ng·mL^{-1}. RSD values were calculated in the range of 0.45–11.5% and the relative recoveries in the wastewater matrix successfully presented a range of 87.5–100.5%.

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Enhanced cup-shaped 3D-printed devices with dual stirring positions for solid-phase extraction of fluoroquinolones

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Keywords: *Fluoroquinolones, Emerging contaminants, 3D-device, Metal-organic framework*

Since penicillin discovery, antibiotics has been one of the greatest advances in both human and veterinary medicine. Fluoroquinolones (FQs) are a family of broad-spectrum antibacterial agents acting against gram-positive and gram-negative, aerobic and anaerobic organisms. FQs are widely used in the treatment of both humans and animals, but because their incomplete metabolism and limited biodegradation, they are discharged into the environment, which supposes reported toxic effects on aquatic organisms and undesirable effects on the human body health. For example, approximately 15–50% of Enrofloxacin (ENR) used ended in aquatic environments. Therefore, the development of effective and selective sample pretreatment methods for FQs from complex samples before their analysis is crucial for monitoring, environmental protection and human health. However, the trace levels of these analytes in environmental waters needs the implementation of novel extraction systems capable of achieving high-preconcentration levels. In this regard, the development of innovative extraction systems becomes crucial for the detection of these compounds. In this sense, the use of 3D-printing, a layer-by-layer manufacturing technique, provides new opportunities for the preparation of tailored devices. Nonetheless, drawbacks, such as the low surface area, force its combination with advanced functional materials, such as metal-organic frameworks (MOFs), which seamlessly complement 3D-printing and enhance its features.

In this work, a 3D-printed device modified with a MOF for FQs retention in water samples has been developed. The 3D-printed cup-shaped device, with a tailored design, containing two stirring positions can provide a preconcentration factor higher than 150. Several MOFs were tested, selecting among them the one based on zinc and trimesic acid ligand (BTC). For this purpose, the cup cavity of the 3D device was conveniently treated to directly grow $Zn_3(BTC)_2$ MOF on them. Different MOF growth strategies, such as direct mix of MOF precursors (zinc and BTC) or layer-by-layer, were tested to obtain an efficient recovery and maximum FQs retentions. This work showcases the extensive potential of preparation of customized designs that are not achievable with other manufacturing techniques, highlighting the possibilities of these devices in the sample preparation field.

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P-78

A chromia-based sorbent for the enrichment of phosphotyrosine biomarker

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Keywords: *Core@shell particles, Dispersive solid-phase extraction, Chromia, Phosphotyrosine*

Developing of new core@shell particles (CSPs) bearing metal oxides on their outer surfaces is of a great interest. Such hybrid systems have many benefits, i.e., low cost, operation simplicity, chemical stability, and tunability along with simple recoverability and reusability that make them suitable as dispersive solid-phase extraction (DSPE) sorbents for selecting/extracting different types of molecular structures. Accordingly, herein, novel chromia-based CSPs were successfully prepared and utilized as efficient DSPE for selective enrichment toward phosphotyrosine (pTyr). A modified version of Stöber method was used to prepare highly dispersed core particles that were further coated with the chromium oxide. The prepared chromia sorbent showed a significant improvement in extracting a probe-analyte (pTyr) compared to the results obtained by titania-based counterparts. As well to this, a noticeable stability of the SiO_2@Cr_2O_3-CSP sorbent was remarkably achieved which upon simple solvent-wash cycles, the studied sorbent can be regenerated/reused. Noticeably low-levels of LOD and LOQ (3.0 and 15 pg·mL^{-1}) were attained with good linearity (R^2 of 0.9995), batch-to-batch reproducibility (RSD% ≤10) and run-to-run repeatability (RSD% ≤5.5).

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P-79

Exploiting natural materials as sorptive phases in rotating-disk sorptive extraction

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Keywords: *Microextraction, Rotating-disk sorptive extraction, Natural sorptive phases, Water*

Rotating-disk sorptive extraction (RDSE) is an equilibrium-based extraction technique and from a kinetic point of view, the rate-determining step of the extraction corresponds to when the analyte crosses the boundary layer of water on the surface of the sorbent. Although this layer is always present, it can be thinned with efficient convection, reaching partition equilibrium faster. This is the main advantage of RDSE over other microextraction techniques where the stirring is slower. The rotation of the disk can reach velocities up to 3000 rpm without damaging the sorbent phase since it is only in contact with the liquid sample [Trac–Trends Anal. Chem. 137 (2021) 116209].
The extraction device used in RDSE corresponds to a small disk (1.5 mm diameter) that has a miniature magnetic bar inserted. It was initially built of Teflon, but other materials have also been described. Two configurations have been described for the disk: (A) a flat disk with a laminar sorbent phase immobilized on one of its surfaces and (B) a disk with a cavity of 0.44 cm^3 into which a portion of particulate sorbent phase (20–80 mg) is loaded and covered with filter paper and sealed with a Teflon ring [Trac–Trends Anal. Chem. 137 (2021) 116209].
Several synthetic sorptive phases have been used in the diverse applications described for RDSE and only two natural phases have been proposed (cork and clay). In both cases, analytical methods have been proposed for determination of trace of emerging and persistent organic contaminants in water, respectively [Trac–Trends Anal. Chem. 137 (2021) 116209].
In a new research project, other natural materials, which normally are agricultural and household wastes, are proposed as sorbent materials, containing functional groups which can interact with organic analytes via different interactions, such as pi-pi electron donor-acceptor, H-bonding, and pore-filling mechanisms. In the present study, some results of characterization and analytical applications are discussed considering natural and modified phases based on chitosan and fruit seeds. In the case of chitosan, this biopolymer was crosslinked with a low concentration of glutaraldehyde to form thin films that were easily immobilized on the surface of the rotating disk. The main advantage of this modification is the considerable decrease in the swelling capacity, which prevents loss and rupture of the sorbent during extraction with high rotation of the disk. In addition, it not only improved the physical characteristics of chitosan but also increased its extraction capacity. This sorbent was applied to the determination of triclosan and methyl-triclosan in water. On the other hand, avocado seed was also assessed as sorptive phase. The natural material and its pyrolyzed product were characterized. The activated carbon shown better properties as sorptive material for contaminants of emerging concern.

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P-80

Simultaneous determination of thyroid hormones in serum using BioSPME for sample preparation

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Keywords: *Solid-phase microextraction, Bioanalytical solid-phase microextraction, Serum, Plasma, Hormones*

The thyroid hormones triiodothyronine, T3 or 3,5,3'-triiodo-l-thyronine, and thyroxine, T4 or 3,5,3',5'-tetraiodo-l-thyroxinine, are biomarkers used to monitor thyroid activity. Approximately 0.04% of the total T3 and 0.02% of the total T4 is available as the free form in circulation, with the remainder bound primarily to thyroxine-binding globulin and, to a lesser extent, albumin and transthyretin [Eur. J. Endocrinol. 175 (2016) R255–R263]. Direct analogue immunoassays, the most common tests performed at most clinical laboratories, suffer from interferences and lack of specificity leading to criticism for poor quality [Clin. Biochem. 44 (2011) 89–94]. The most accepted sample preparation for determining the free concentration of these hormones involves the lengthy process of equilibrium dialysis prior to quantification by LC-MS/MS.
This work presents a novel approach to accurately monitor and determine the free T3 and T4 in under an hour of sample preparation using a technique called BioSPME, bioanalytical solid-phase microextraction, prior to analysis by LC-MS/MS. The BioSPME device is a 96-pin array with a 2 mm coating of C_{18} silica particles in a biocompatible binder on the outside of each pin. This device operates by direct immersion into the sample solution, washing solutions or extraction solutions and requires no active pipetting.
During method development for sample preparation various parameters such as choice of organic modifier, pH value as well as extraction, washing and desorption times have been investigated and optimized. The method was tested for reproducibility using reference standards and serum samples. The accuracy of the results was checked versus a validated method using equilibrium dialysis and LC-MS/MS. The new method allows the simultaneous determination of free T3 and T4 hormones. BioSPME reduces the sample preparation time from several hours (equilibrium dialysis) to less than an hour.

P-81

Metal-organic framework-modified paper-based for extraction of neonicotinoids in water samples

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Keywords: *Metal-organic framework, Paper-based device, Micro-solid-phase extraction, Neonicotinoids, Cellulose*

Neonicotinoids (NEOs) are a type of synthetic insecticides that have gained recognition for their effectiveness in controlling pests in diverse agricultural crops. However, due to their hydrophilic nature, persistence and widespread application, residues of these can readily migrate from agricultural practices to various environmental matrices, causing severe effects. Consequently, there is a significant need to regulate and control the presence of NEO residues in agricultural samples to safeguard living organisms. Therefore, the development of highly sensitive analytical methods becomes crucial for the accurate monitoring of these compounds. In this regard, considerable efforts are being made to advance the development of novel materials with enhanced sorbent properties.
Metal-organic frameworks (MOFs) are a group of microporous materials studied in the field of analytical chemistry due to their captivating characteristics, including a high surface area, exceptional porosity, customizable topology, and easy functionalization. However, their use in sustainable platforms such as paper-based devices is a relatively unexplored field. Paper, as a substrate, presents several advantages such as biocompatibility, non-toxicity, versatility, flexibility and low-cost. In this work, a paper-based device modified with MOF is described for the extraction of five NEOs (thiamethoxam, clothianidin, imidacloprid, acetamiprid, and thiacloprid) followed by their determination by HPLC with diode-array detection. For this purpose, the cellulose paper was subjected to carboxymethylation, to allow the coordination of metal ions and initiate the growth of the MOF. Also, a green route of the selected MOF (MIL-53 (Al)) was carried out. One-pot and layer-by-layer were also investigated, providing the latter one the best results in terms of extraction performance. The MOF-modified paper-based was also characterized by FTIR, SEM and XRD. Besides, the extraction process was optimized by investigating variables such as pH and ionic strength of the sample, extraction and desorption times, nature and volume of desorption solvent, among others. Under optimized conditions, suitable recoveries (> 75%, except for thiamethoxam) were obtained and satisfactory limits of detection. The developed method was successfully applied to the determination of these NEOs in different water samples.

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YOUNG POSTER COMMUNICATIONS

YP-01

In-vitro bioaccesability of hazardous chemicals coming from rubber recycled tire using simulated biological fluids

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Keywords: *Recycled crumb rubber, Solid-phase extraction, Hazardous compounds, Biological samples, Liquid-chromatography-mass spectrometry*

Tire rubber is made-up by many organic compounds that give the properties making the tire resistant and durable. These organic compounds can migrate to the environment thought particles that are used on many fields in order to give a second life to end-of-life tires. The ubiquity of crumb rubber employed in many applications: football fields, playgrounds for kid or gym floors can result as a high exposure for human beings, especially for children playing in these crumb rubber surfaces. This makes necessary to evaluate the quantity of dangerous chemicals in the material, but it is also important to assess their bioaccesability.
Several studies have reported that PAHs (polycyclic aromatic hydrocarbons) are present in this material [Chemosphere 90 (2013) 423-431] and recently their bioaccesability has been shown [Sci. Total Environ. 857 (2023) 159485]. Other hazardous organic compounds such as the antioxidant, 6PPD (N-(1,3-dimethylbutyl)-N′-phenyl-p-phenyl-enediamine) and the 6PPDq (N-(1,3-dimethylbutyl)-N′-phenyl-p-phenyl-enediamine-quinone), ozonation product of 6PPD, are in the spotlight due to their toxicity for the aquatic life being related with coho salmon's death [Science 371 (2021) 185–189]. Other families of compounds such as crosslinkers like HMMM (hexamethoxymethyl melamine), vulcanizants, like MBTZ (2-mercaptobenzothiazole) can be present and could have toxic effects for humans and the environment.
This work describes a methodology to study the bioaccesability of twelve compounds in biological fluids in contact with recycled crumb rubber. The biological fluids (saliva, gastric, duodenal and bile) are prepared in accordance with the UBM procedure [BARGE-INERIS, 2010]. The analytical method consists of the extraction of the compounds from the gastric fluids using solid-phase extraction (SPE) and the identification and quantification are carried out by liquid chromatography tandem mass spectrometry analysis. First, preliminary experiments were performed in order to achieve the best extraction conditions, such as the sample volume and elution solvent. The study of simulated fluids in contact with crumb rubber showed the human bioaccesability of some of the target toxic compounds.

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YP-02

Particles from tire rubber: Determination of hazardous chemical agents

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Keywords: *Recycled crumb rubber, Ultrasound-assisted extraction, Hazardous chemicals, Sample preparation, Liquid chromatography-mass spectrometry*

Many chemical agents are added to tire rubber to provide durability and resistance. A way of recycling end-of-life tires is by shredding them. The crumb rubber obtained, considered as a microplastic, is used as infill in artificial turf sport fields and as playground paving [Chemosphere 195 (2018) 201–211]. Vulcanizing and crosslinking agents are chemicals of interest due to their possible environmental and human health implications [Sci. Total Environ. 802 (2022) 149799; Environ. Pollut. 287 (2021) 117659]. Moreover, the antiozonant 6PPD (N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine) and one of its transformation products, 6PPDq (N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine-quinone), whose presence in aquatic environment seems to be related to the mortality of the coho salmon, are also included in this investigation [Science 371 (2021) 185–189].
In this work, an analytical methodology has been developed for the simultaneous detection and quantification of the previously mentioned antiozonant 6PPD and its degradation product, 6PPDq, as well as vulcanizing and crosslinking agents in crumb rubber, based on ultrasound-assisted extraction (UAE) followed by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). After optimizing the solvent and the temperature of extraction, the method UAE-LC-MS/MS was validated in terms of analytical performance. Finally, it has been applied to a wide variety of real samples, including crumb rubber from football fields and playgrounds, to determine the presence and concentration of these compounds. In addition, several alternative materials were also analyzed with comparative purposes. The antiozonant 6PPD achieved the highest concentration levels in new synthetic fields, reaching concentrations up to 0.2% w/w.

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YP-03

Determination of hazardous compounds from tire rubber in water using solid-phase microextraction (SPME)

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Keywords: *Recycled crumb rubber, Solid-phase microextraction, Hazardous chemicals, Sample preparation, Gas chromatography-mass spectrometry*

Tire rubber is made up of many chemicals and some of them are considered environmental pollutants. These chemical agents can enter aquatic ecosystems directly through tire wear particles and indirectly through water leachates from artificial turf sport fields and playground paving made of recycled crumb rubber [Chemosphere 270 (2021) 128610]. Some of these substances are the antiozonant 6PPD (N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine) and one of its transformation products, 6PPDq (N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine-quinone), which seems to be linked to the mortality of the coho salmon in the Pacific [Science 371 (2021) 185–189]. Vulcanizing and crosslinking agents, such as HMMM (hexamethoxymethyl melamine), are also compounds of interest due to their possible environmental and human health implications [Sci. Total Environ. 802 (2022) 149799; Environ. Pollut. 287 (2021) 117659].
The objective of this work is the development of an analytical method for the simultaneous detection and quantification of the previously mentioned emerging contaminants, such as the antiozonant 6PPD and its degradation product 6PPDq, as well as vulcanizing and crosslinking agents from tire rubber in water. The method is based on solid-phase microextraction (SPME) followed by gas chromatography coupled to tandem mass spectrometry (GC-MS/MS). Different parameters affecting SPME were optimized to achieve an efficient methodology for all the target analytes. The optimization was carried out by an experimental design in which the extraction mode, temperature, fibre coating and salting-out effect were evaluated. Once the method was validated, it was applied to real water samples put in contact with rubber material, some of them recollected from football fields and playgrounds. Some of the target compounds, including 6PPDq, were found in the real waters demonstrating their leaching from the rubber.

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YP-04

Extraction of emerging organic pollutants from polyethylene and polypropylene microplastics

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Keywords: *Microplastics, Emerging organic pollutants, Environmental samples, Liquid chromatography, Mass spectrometry*

Plastics are, without a doubt, one of the most important materials that have been introduced in the last century. However, due to inadequate waste management, a significant part of them ends up in the environment, where they suffer several degradation processes (chemical, physical and/or biological) that end up producing the formation of smaller plastic particles, known as microplastics (MPs) when they have a size between 1 µm and 5 mm in their largest dimension. Their polymeric nature, along with their large surface area, provide MPs with the ability to retain contaminants on their surface through different mechanisms (mainly adsorption), pre-concentrating them and protecting them against different environmental degradation processes that would affect their persistence. For this reason, in recent years, the study of the presence of contaminants in MPs has experienced growing interest in the scientific community; however, many of these studies have focused mainly on persistent organic pollutants, leaving aside others such as emerging organic pollutants [Trac–Trends Anal. Chem. 136 (2021) 116186].
In this work, a vortex-assisted extraction method of 19 emerging contaminants (including phenols, antibiotics, estrogens, and pharmaceuticals) was optimized and validated in different types of MPs (polyethylene and polypropylene, both in pristine conditions and weathered). The determination was carried out by ultra-high performance liquid chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS). The proposed method showed good recovery values, mostly between 70 and 120%, with relative standard deviations less than 20%. Furthermore, the method was successfully applied to the analysis of real environmental MPs collected in different hotspots of microplastic arrival located in the Canary Islands.

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YP-05

Untargeted screening and risk assessment of semi-volatile organic compounds in Spanish household dust: Pilot study

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Keywords: *High-resolution mass spectrometry, Indoor dust, Risk assessment, Semi-volatile organic compounds, Untargeted analysis*

According to the World Health Organization, household air pollution was responsible for approximately 3.2 million deaths per year in 2020, including over 237,000 deaths of children under 5 years old, all over the world. Different respiratory and cardiovascular diseases are leaded to the household air pollutants exposure. Household air pollution involves particulate matter (PM), inorganic chemical pollutants (ozone, carbon monoxide, sulfur dioxide, etc.), organic chemical pollutants (toluene, xylene, styrenes, flame retardants compounds, etc.), and other biological pollutants, such as moulds. In this way, pollutants and substances that are known to be present in the air can be found in household dust, which acts as reservoir, posing a potential risk to human health.
Household dust is a complex pollutant mixture composed of pollen, particulate matter, dead skin cells, insects, several fibers (both natural and synthetic), and other indoor materials from furnishing and floor. Currently, adult population spends long time in indoor environments and, in consequence, they are exposed to indoor dust. For this reason, a significant number of studies have been performed to demonstrate the presence of different pollutants in this complex matrix.
In this work, a novel analytical approach has been conducted for the untargeted screening of semi-volatile organic compounds in Spanish household indoor dust samples. The method was based on a microwave-assisted extraction followed by gas chromatography coupled to high-resolution mass spectrometry using a hybrid quadrupole-orbitrap analyzer. The acquisition was performed in full scan mode with a resolution of 60,000 FWHM, and a mass range from 40 to 500 m/z. The acquired data were processed using the Compound Discoverer™ 3.3 software. The method was applied to 19 residential indoor dust samples, collected in different Spanish regions (namely Galicia, La Rioja, Catalunya, the Balearic Islands, and the Valencian Community). From the generated data, 4067 features were annotated, of which 474 compounds were tentatively identified with a high level of identification confidence, using a restrictive set of identification criteria. Most of them were natural products, metabolites, additives, and substances with industrial applications in the field of foods, cosmetics, pharmaceuticals, pesticides, and plastics. Finally, the risk assessment was carried out by applying the threshold of toxicological concern approach, showing that risk to adult population associated with the presence of the identified substances in the household dust was not expected in average indoor conditions, although the existence of indoor environments with conditions of potential risk cannot be discarded.

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YP-06

Vacuum headspace solid-phase microextraction analysis of pesticides in grapes

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Keywords: *Solid-phase microextraction, Vacuum solid-phase microextraction, Grapes, Pesticides, Extraction methods, Gas chromatography mass spectrometry*

The utilization of grapes in their unprocessed state and their derived products as part of daily dietary consumption is a commonly observed factor contributing to human intoxication caused by the presence of pesticide residues [Food Chem. 274 (2019) 291–297]. These pesticides are classified into distinct categories including insecticides, herbicides, fungicides, and zoocides, which further fall into subcategories such as organophosphates, triazoles, peritroids, and multi-classes [J. Food Compos. Anal. 95 (2021) 103695; Foods 11 (2022) 1623]. It is crucial to develop dependable, sensitive, and cost-effective analytical approaches that can cover a broad range of pesticides for the purpose of risk assessment and the study of residue levels in grapes. Traditionally, conventional extraction methods [Food Res. Int. 133 (2020) 109141; J. Chromatogr. A 1433 (2016) 1–23] have been employed to extract pesticides; however, due to the diverse chemical structures and physico-chemical properties of these compounds, this task is extremely challenging. Therefore, in this study, we propose the vacuum headspace solid-phase microextraction (Vac-HS-SPME) method to determine the quantity of pesticide residues in grape. This method enables the simultaneous analysis of six pesticides from various classes, namely boscalid, quizalofop-p-methyl, oxyfluorfen, fluroxypyr, metribuzin, and epoxycenazole. By using a response surface methodology, we investigated the impact of independent variables, such as extraction temperature (30-80 °C), extraction time (1-20 min), fiber coating (CAR/PDMS/DVB and PEG), desorption time (1-5 min), and vacuum time (60-120 s), with the objective of achieving lower detection limits (0.1-300 µg/L) and shorter analysis times. Gas chromatographic separation was accomplished using a SLB-5ms column (30 m x 0.25 mm, 0.5 µm). The results clearly demonstrated that the combination of Vac-HS-SPME proved to be more appropriate and selective for the extraction of pesticides from grapes. In fact, the use of Vac-HS-SPME exhibited superior performance, with detection limits 3-10 times lower than those of classical SPME and SPE methods, while also requiring less sampling time under the same extraction conditions. Moreover, we propose a vacuum headspace solid-phase microextraction (Vac-HS-SPME) method followed by gas chromatography-mass spectrometry (GC-MS) for the precise and quantitative determination of pesticides in grapes.

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YP-07

Optimization of an extraction procedure to assess contaminants of emerging concern in freshwater invasive species

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Keywords: *Contaminants of emerging concern, Ultrasound solvent-assisted extraction, Aquatic biota, High-resolution mass spectrometry, Invasive species*

Detection and monitoring of contaminants of emerging concern (CECs) in freshwater samples have gained significant importance in recent years due to the potential risks they pose to the environment. Analyzing CECs in aquatic organisms can provide valuable insights into the cause-and-effect relationships, surpassing the limitations of measuring discrete levels in water or sediment samples alone. Invasive species, similar to native fauna, can serve as effective bioindicators for assessing mixtures of chemical exposure in freshwater ecosystems, as they often exhibit greater tolerance to environmental stresses. Currently, the majority of biomonitoring efforts for CECs have focused on fish and mussels, with only a few studies examining invasive species. Furthermore, these studies have primarily concentrated on a limited number of specific compounds or a particular family of compounds.
In this sense, an efficient extraction method was developed to detect a wide range of CECs in four different species inhabiting the Valencian Albufera (Spain), including three invasive freshwater species (*Procambarus clarkii, Corbicula fluminea, Lepomis gibbosus*) and one native species (*Anodonta cygnea*). The targeted compounds encompassed 87 pharmaceutically active compounds, 11 organophosphorus flame retardants, 21 perfluoroalkyl substances, and 55 pesticides. Liquid chromatography coupled with high-resolution mass spectrometry was used to perform the analysis by full scan followed by data-independent-acquisition (DIA).
We optimized the ultrasound solvent-extraction method using four different extraction solvents: A. Acetonitrile + 0.1% formic acid (FA), B. mix of isopropanol with acetonitrile (1:3) + 0.1% FA, C. water:methanol (70:30) + 1% FA, and D. 100% methanol. Additionally, three dispersive solid-phase extraction (d-SPE) were tested to clean the extracts and reduce the matrix effect: A. Z-Sep, B. Z-Sep$^+$, and C. Z-Sep/C_{18}. The performance of the methodology was evaluated in terms of recovery efficiency, accuracy, and linearity.
Among four different solvents tested, acetonitrile acidified with 0.1% formic acid was chosen as the best extraction solvent due to its superior performance in yielding the highest recoveries, higher accuracy, and fewer matrix effects for most compounds and matrices, and Z-Sep/C_{18} was selected by clean-up.
In brief, the extraction procedure optimized was as follows: 0.5 g of soft tissue was weighed and placed in a 2 mL Eppendorf tube. To homogenize, two stainless steel beads were added, and the sample was processed using a TissueLyzer sample disruptor. Next, 1 mL of acetonitrile + 0.1% FA was added and underwent ultrasound for 10 min. Subsequently, it was centrifuged, and 750 µL of the supernatant was transferred to a vial containing Z-Sep/C_{18}. The supernatant was transferred in an HPLC vial and it was evaporated to dryness and reconstituted in 500 µL of H_2O (5 mM ammonium acetate) and MeCN (90:10) for HPLC-MS/MS analysis.
The developed method was validated at two concentration levels (10 and 100 ng·g^{-1}). All samples were prepared in triplicate to ensure accuracy and reproducibility. Most target analytes exhibited recovery rates between 40 and 120%, with a relative standard deviation of less than 20%. Low limits of quantification (LOQs) were achieved for most compounds across all matrices studied, ranging from 0.01 to 22 ng·g^{-1}.
Subsequently, the validated analytical method was successfully applied to analyze the select contaminants in wild species captured in the Albufera Natural Park (Spain). The results revealed the presence of CECs in all samples. Notably, compounds such as acetaminophen (C_{max} 10 ng·g^{-1}), hydrochlorothiazide (C_{max} 0.42 ng·g^{-1}), tramadol (C_{max} 0.86 ng·g^{-1}), PFOS (C_{max} 60 ng·g^{-1}), carbendazim (C_{max} 4 ng·g^{-1}), and fenthion (C_{max} 52 ng·g^{-1}) were detected, predominantly in the Asian clam (*Corbicula fluminea*).

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YP-08

Multisorbent extraction and HRMS DIA based quantification method for the analysis of wastewater-borne pollutants in temporary rivers

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Keywords: *Contaminants of emerging concern, Pharmaceuticals, Solid-phase extraction, Multilayered-multi-sorbent cartridges, High-resolution mass spectrometry*

Temporary rivers are defined by seasonal flooding and drying, where climate and geomorphic characteristics have a direct influence on structural and functional features. Effluents from industrial and municipal wastewater treatment plants (WWTPs) are a continuous source of contamination to surface water and temporary rivers can receive important contributions from these, accounting even for the totality of the river flow, especially during the dry season. WWTPs are not fully efficient in the removal of several compounds, consequently, water soluble compounds, among these pharmaceuticals, can be detected in surface water at concentrations up to µg/L. These can accumulate and induce unintended effects in nontarget organisms. Hence, the determination of these compounds in the environment is essential to characterize the quality of surface water and the changes that can undergo. In this study, the aim was to develop an extraction and quantification method for wastewater-borne pollutants in surface water and to study the effect of different WWTP discharges along the watercourse of temporary rivers in Spain.
A robust method was developed for the quantification of popular and highly occurrence contaminants of emerging concern (CECs) from wastewater treatment plant effluents. A total of 116 CECs of different classes were selected based on their occurrence, high consumption and compounds included in the EU Watch list. The representative selection of compounds covered a wide range of polarities with log P values ranging from -2.16 to 5.26 and different physicochemical properties. A homemade multi-layered and multi-sorbent solid-phase extraction (SPE) cartridge was used to cover the wide range of polarities of the selected contaminants. As for the elution protocol, a non-discriminant elution protocol was applied. The elution protocol consisted on 2 x 3 mL 5% ammonia in methanol:ethyl acetate (50:50 v/v), followed by 2 x 3 mL of 2% formic acid in methanol:ethyl acetate (50:50 v/v) and finally 3 mL of methanol:ethyl acetate (50:50 v/v). Liquid chromatography coupled to a high-resolution mass spectrometer (HRMS) Q-Exactive Orbitrap-MS system was used for the separation and detection of the contaminants. A targeted analysis using the data independent acquisition (DIA) mode with an inclusion list with the exact mass, retention time window and collision energy was tried for the first time obtaining good sensitivity, selectivity and high quality MS^2 product ions. The 116 compounds of a wide-scope of polarities and physicochemical properties were validated using a surface water pool matrix and at three concentration levels 5, 50, 500 $\mu g \cdot L^{-1}$ in extract. Good recoveries were obtained between 70 and 120% for the majority of the selected contaminants. Matrix effect, precision, and linearity were also evaluated and results proved the suitability for the method application for wastewater-borne pollutants in surface water.

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YP-09

Extraction of emerging organic pollutants from seawater and wastewater from Tenerife (Canary Islands, Spain) using an automated solid-phase extraction system

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Keywords: *Emerging organic pollutants, Environmental water samples, Automated solid-phase extraction, Liquid chromatography, Mass spectrometry*

In the last decade, there has been a notable interest in the determination of emerging organic pollutants, a group of substances that present a risk to the environment and human health, even at low concentrations, and which legislation is not yet widely developed, which explains the generalized lack of current regulations for many of them. In fact, many of these contaminants have recently begun to be detected thanks to the advances that Analytical Chemistry has experienced in recent years. Consequently, the impact and incidence of these compounds in the environment is still not completely known and there is little information regarding their persistence, hence the development of studies focused on their determination in environmental samples is of great interest [Sci. Total Environ. 408 (2021) 6062–6069].
In this work, the determination of 17 emerging organic pollutants in samples of seawater and wastewater from the island of Tenerife (Canary Islands, Spain) has been carried out. The selected analytes included 3 phenols, 1 antibiotic, 8 estrogens, 3 pharmaceuticals, and 2 consumption habits compounds. Extraction was carried out by automated solid-phase extraction using reverse phase Strata™-X polymeric cartridges (500 mg, 6 mL, 33 µm) using acetonitrile as elution solvent. For the determination of the analytes, an ultra-high efficiency liquid chromatography equipment coupled to a tandem mass spectrometry detector was used, employing a HPH-C_{18} column (50 x 2.1 mm, 2.7 µm). Overall, the method provided good recovery values for most of the analytes in both samples with values ranging from 60-120% with relative standard deviations lower than 20% for most of them.

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YP-10

Determination of 11 antibiotics in fish samples by QuEChERS-UHPLC-MS/MS

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Keywords: *Antibiotics, Fish muscle samples, QuEChERS, Liquid chromatography, Mass spectrometry*

Fish are an important food source due to their high nutritional values and health benefits. In response to the increasing demand, fish farming has become one of the fastest growing sectors of the food industry, globally. To prevent the dissemination of bacterial infections, the use of antibiotics has gained an important role. From their discovery in the 20th century, antibiotics have saved countless lives, making them one of the great milestones of modern medicine. Nevertheless, the overuse of these substances has become a tangible problem from an environmental point of view, but also due to the nefarious effects on human health associated, as the increasing antibiotic resistance of bacteria could potentially render many antibiotics ineffective. This increase in resistance poses an alarming threat for public health, as the efficacy of different treatments may be jeopardized, which highlights the importance of a responsible use of antibiotics and the development of new strategies to minimize antibiotic resistance [J. Infect. Public Health 10 (2017) 369–378].
In this work, the determination of 11 antibiotics in muscle samples of European sea-bass and gilt head bream (cultured in Tenerife, Canary Islands, Spain) has been carried out. The antibiotics studied include 6 quinolones, 2 sulfonamides, 2 diaminopyrimidines and 1 macrolide. Extraction was carried out using the QuEChERS method after homogenization of the fish muscle previously frozen with liquid nitrogen. For the determination of the analytes, an ultra-high performance liquid chromatography equipment coupled to a tandem mass spectrometry detector was used, employing a C_{18} column (100 x 3.0 mm, 2.7 µm). The validated method provided good recovery values (60-120%) and low relative standard deviations (< 20%). A total of 10 samples of each species were also analyzed.

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YP-11

Exposure and risk assessment to airborne dl-PCBs, dioxins and furans in the population living in the neighborhood of a cement plant: A pilot study in the Valencian Region (Spain)

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Keywords: *Dioxins, Ambient air, Risk assessment, Cement plant, Cancer risk*

Emissions from cement manufacturing facilities may increase health risks in nearby populations. For this reason, dioxin-like PCB (dl-PCB), polychlorinated dibenzo-p-dioxin (PCDD), and polychlorinated dibenzofuran (PCDF) concentrations in PM_{10} samples were assessed in the vicinity of a cement manufacturing plant located in the Valencian Region (eastern Spain). The total concentrations of the sum of airborne dl-PCBs, PCDDs, and PCDFs ranged between 1.85 and 42.53 fg TEQ/m^3 at the assessed stations.
Regarding the exposure, the average daily inhalation dose (DID) for the sum ranged from $8.93 \cdot 10^{-4}$ to $3.75 \cdot 10^{-3}$ pg WHO TEQ·kg^{-1} b.w.·day^{-1} in adults, and from $2.01 \cdot 10^{-3}$ to $8.44 \cdot 10^{-3}$ pg WHO TEQ·kg^{-1} b.w.·day^{-1} in children population. Risk assessment for adults and children was performed using both daily and chronic exposure. The hazard quotient (HQ) was calculated considering 0.025 pg WHO TEQ·kg^{-1} b.w.·day^{-1} to be the acceptable maximum permitted inhalation exposure. The HQ obtained was slightly higher than 1 for PCDD/Fs at one of the stations, indicating a possible health risk for the population under study due to inhalation exposure. In the case of chronic exposure, cancer risk (>10^{-6}) was observed for some samples in also one of the assessed sampling sites.

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YP-12

PFASs in paper- and cardboard-based food contact materials

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Keywords: *Per- and poly-fluoroalkyl substances, Food contact materials, Ultrasound-assisted extraction, Liquid chromatography, High-resolution mass spectrometry*

Per- and poly-fluoroalkyl substances, commonly known as PFASs, are organofluorine compounds which contain at least a completely fluorinated methyl (-CF_3) or a methylene carbon atom (-CF_2-). PFASs are widely used in daily life applications and products thanks to their chemical and thermal stability as well as their resistance to moisture and oil. Hence, PFASs coatings are found in fire extinguishers, textiles, and paper. However, PFASs with long chain are considered persistent pollutants due to their bioaccumulation and harmful effects on human health. Therefore, PFASs on paper- and cardboard-based food contact materials (FCM) have a special interest because of their migration into food poses a potential risk to human health.
In this study [Anal. Methods 15 (2023) 1559–1568], a green analytical method for the determination of 21 PFASs in paper- and cardboard-based FCM was developed and validated according to Commission Recommendation (EU) 2019/794 [https://data.europa.eu/eli/reco/2019/794/oj], which encourages the determination of the total content of PFASs in FCM, instead of just determining their migration into food simulants. For that, paper- and carboard-based FCM samples were chopped, spiked with internal standards and PFASs were extracted using a fast and simple green ultrasound-assisted solid-liquid extraction (lixiviation), using a mixture of acetonitrile and water as extraction solvent. Finally, the analysis was carried out by liquid chromatography coupled to high-resolution mass spectrometry (LC-Q-Orbitrap HRMS) in full scan/data-dependent MS^2 mode (FS/ddMS^2). In order to reduce background PFASs contamination, all the glassware materials were rinsed with acetone before their use and plastic materials containing PTFE were avoided. Moreover, to control background PFASs contamination, procedural blanks and reagent blanks were also prepared.
Otherwise, taking into account the eco-friendly characteristics of this methodology according to the Analytical Eco-Scale [Trac–Trends Anal. Chem. 37 (2012) 61–72], it might be considered an excellent green analysis (Eco-Scale score >75).
Finally, 16 paper- and cardboard-based FCM, such as pizza boxes, boxes for potato fries, ice cream tubs, and cardboard packaging for cooked Spanish omelet, fresh grapes, and frozen fish and salads, were analysed, showing that they were in accordance with current European regulations.

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YP-13

Identification of unknown substances in the ambient air of medical care centers surroundings in the Valencian Region (Spain)

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Keywords: *Ambient air, Unknown analysis, Tentative identification, High-resolution mass spectrometry*

Healthcare facilities such as hospitals and health centers have been shown to be important emission points for chemical compounds from operating theatres and ventilation system of different hospital areas. Nevertheless, the impact of these pollutants on the urban population and more specifically near urban health facilities has not been assessed. A new strategy has been applied to identify unknown substances in the atmosphere of the surroundings of two different hospitals in the Valencian Region (Spain) during the sixth wave-COVID period (January-February 2022). Air samples (particulate phase and gaseous phase) were collected using a low-volume sampler (Digitel DPA-16) with a sampling flow of 2.3 $m^3 \cdot h^{-1}$ for 72 hours, collecting around 170 m^3. A generic extraction methodology using microwave-assisted extraction (MAE) and ethyl acetate as solvent was employed. The collected samples were analyzed using two different instruments: LC-HRMS-Tribrid system and GC-QExactive-HRMS. More than 300 substances were tentatively identified using restrictive criteria regarding exact mass, retention time, isotopic profile and MSn spectra. These substances belonged to different chemical groups like pesticides, phthalates or PAHs and different origin sources like medicine, industrial or cosmetics products.

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YP-14

Optimization of a solid-phase extraction procedure to determine a wide range of per- and polyfluoroalkyl substances (PFAS) by LC-HRMS in drinking waters from the Basque Country

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Keywords: *Per- and poly-fluoroalkyl substances, Solid-phase extraction, Liquid chromatography, High-resolution mass spectrometry, Drinking water*

Per- and polyfluoroalkyl substances (PFAS), also known as “forever chemicals”, are an upcoming threat to the environment and living beings due to their toxic effects together and high bioaccumulation capacity. These compounds have unique properties such as high chemical and thermal stability as well as their ability to repel both water and oil that make them highly valuable in a wide range of industrial applications (i.e., polymer manufacture, food-contact materials, fire-fighting foams, textile treatments, etc.). However, due to these properties, PFAS are very persistent and difficult to degrade, which makes them prone to long-distance transport through different environmental compartments. In this way, water is one of the pathways that could increase human exposure to PFAS which led the regulatory bodies to establish a maximum allowed concentration of PFAS in drinking water. Due to the risk posed to human health, since January 2021 the EU Drinking Water directive established a limit of 0.1 µg/L for the sum of a selection of 20 PFAS or 0.5 µg/L for all PFAS. Moreover, the regulation tendency is to decrease these limits even further, such as in Denmark, where the sum of PFOA, PFOS, PFNA and PFHxS cannot exceed 2 ng/L since June 2021, or recently (March 2023) the American Environmental Protection Agency, who proposed the maximum contaminant level of 4 ng/L for PFOA and PFOS in drinking waters. However, the vast number of PFAS (more than 7000) and the high differences in the chemical structure they have, extremely complicated to carry out a wide range determination of these compounds and at such low levels.
Thus, the main goal of this work has been the optimization of a solid-phase extraction (SPE) procedure to achieve the determination of a wide range of PFAS in tap drinking water from the Basque Country by liquid chromatography coupled to high-resolution mass spectrometry (LC-HRMS). To do so, four different SPE procedures were compared: two procedures using weak anion exchange cartridges (Oasis WAX), one procedure using a hydrophilic-lipophilic balanced (HLB) cartridge and one protocol using a home-made cartridge including WAX and HR-X phases. The best extraction procedure was then reoptimized to increase the recovery using different solvents for the elution step. Additionally, the heated electrospray (H-ESI) source conditions as well as the chromatographic separation were also evaluated to enhance the performance of the methodology. For that, the influence of the temperatures as well as the capillary voltage and the S-lens radiofrequency level over PFAS’ responses were checked whereas different modifiers were tested to improve the chromatographic separation in a reversed-phase C_{18} column. The method was later validated in terms of precision, trueness, linearity, and detection capability, allowing the detection of a wide range of PFAS down to the ng/L levels in tap drinking water samples.

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YP-15

Target and suspect screening analysis of water-accommodated fractions of crude oil using HS-SPME-GC-MS

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Keywords: *Crude oil, Water-accommodated fraction, Headspace solid-phase microextraction, Gas chromatography, Low-resolution mass spectrometry*

Chemical and oil spills constitute a worldwide threat due to the hazardous effect they could have on the environment and living beings. These oil spills cause the transference of some chemicals to seawater, leading to the so-called water-accommodated fraction (WAF). The analysis of WAF coming from crude oil represents a preliminary step in the preparation of methods to achieve the main objectives of the AMMONTOX project. The overall objectives are: (a) to gain knowledge and develop methods for testing oil toxicity in terms of adverse outcomes; (b) to identify and characterize individual hidden compounds and mixtures contributing to the toxicity of aqueous fractions of oil in seawater; and (c) to develop novel strategies based on the whole-mixture toxicity approach for risk and impact assessment of waterborne oil pollution. Exposure of marine species to dissolved compounds from crude oil can lead to physiological and ecological alterations. Thereby, linking the observed effects to the causative compounds is a priority.
To do so, in this work, we aimed to determine the volatile fraction of low energy WAFs (LEWAF) coming from two different types of crude oil by headspace solid-phase microextraction (HS-SPME) coupled to gas chromatography-mass spectrometry (GC-MS). The LEWAFs were prepared according to guidelines established by CROSSERF [Mar. Pollut. Bull. 40 (2000) 1007–1016]. This experiment was conducted to transfer compounds from the oil to the seawater phase by solubilization only, and trying to reproduce the natural processes that take place in an environmental setting. First, two different SPME fibres were evaluated to ensure the extraction of the highest number of compounds coming from the WAF including those that must be monitored according to CROSSERF as well as those coming from the so-called unresolved complex mixture (UCM). Thus, the proposed methodology was validated and applied to the quantification of the key components coming from crude oils. Moreover, the chemical characterization of potentially hazardous compounds coming from the UCM was also achieved using a workflow based on Schymanski's scale that has been developed to increase confidence in the annotation of the compounds detected in the LEWAF by HS-SPME-GC-MS [Environ. Sci. Technol. 48 (2014) 2097–2098].

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YP-16

Determination of lambda-cyhalothrin in air and its metabolites in urine after conventional and innovative applications in citrus and vineyard crops

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Keywords: *Pesticide, Air, Metabolites, Urine, Cropping systems*

A total of 350,000 tons of pesticide were sold in France, Spain, Italy and Germany during the period 2011-2020, covering this amount two-thirds of the total pesticide sales in the European Union (EU) [EUROSTAT 2022]. The aforementioned countries are known to be the main agricultural producers in the EU and consequently, the most pesticide consumer countries in EU. Thus, the intensive use of pesticides could produce health adverse effects due to human exposure during agricultural application and also due to drift effect. This work shows results from an European LIFE project called Pesticide Reduction using Friendly and Environmentally Controlled Technologies (PERFECT LIFE). The main objective of the project was to demonstrate the reduction of environmental pesticides contamination using optimized application techniques based on Optimal Volume Rate Adjustment tools (OVRA) and drift reducing tools (SDRT) [perfectlifeproject.eu]. Different pesticide application assays were performed in vineyard and citrus crops in two different European countries, Italy and Spain, respectively. Conventional and optimized systems were used to apply lambda-cyhalothrin pesticide during field trials where air samplers and human volunteers (acting as operators and bystanders) were directly exposed to this pesticide. Two types of samples were collected from these assays: (i) air samples which were analysed by gas chromatography coupled to high-resolution mass spectrometry (GC-HRMS); (ii) and volunteer's urine samples, from which two pesticide metabolites, 3-phenoxybenzoic acid (3-PBA) and [3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethyl-cyclopropane carboxylic acid (CFMP), were analysed using liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). Results from air samplers exposed in citrus field trials provide results ranged from 104.93 to 7.61 ng/m^3 after conventional treatments and from 10.93 to 2.15 ng/m^3 after optimized treatments. Similarly, in vineyard crops, pesticide concentration in air after conventional treatment ranged from 14.46 to 3.22 ng/m^3 while after optimized treatment values were from 3.22-0.27 ng/m^3. Regarding pesticide metabolites in urine, it was seen that concentrations of 3-PBA metabolite do not provide a clear reduction trend of its concentration if optimized treatment was used. However, analyzing the specific biomarker (CFMP), urine concentrations increase to a lesser extent if SDRT and OVRA tools were used.

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YP-17

Microplastics determination in soils of Teide National Park (Tenerife, Canary Islands, Spain)

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Keywords: *Plastic pollution, Soil contamination, High mountain environment, H_2O_2 digestion, NaCl flotation*

Plastic pollution has arisen as a global menace due to the huge production and consumption of plastics worldwide, as well as their inefficient end-of-life management, becoming contaminants to the environment. Marine ecosystems have been traditionally identified as sinks of plastics, since the oceans interconnect the world and also cover most of the Earth's surface. Recently, plastic pollution in other environmental compartments have also caught the attention of the scientific community. Thus, on the one hand, the occurrence of microplastics in soils and their associated ecological implications have been attracting attention during the last years. More concretely, an important part of recent research has focused on soils submitted to prolonged agricultural activities since they have been identified as the main source of plastics [Agriculture 12 (2022) 1162]. On the other hand, the detection of microplastics on places far from human activities have also been studied, e.g., in snow collected from virgin and/or remote areas such as national parks and geographically isolated places with difficult accesses [Sci. Total Environ. 873 (2023) 162276].

In this study, we aimed to determine the presence of microplastics in soils of Teide National Park, a 189.9 km^2 area located in Tenerife (Canary Islands, Spain) where lies Mount Teide, which is the highest Spanish mountain and also the highest volcano in the Atlantic Ocean islands. This enclave experiences significant tourist activity, although certain untouched areas are still safeguarded from extensive human interventions. To evaluate the occurrence of microplastics in the whole park, a total of 78 soil samples were collected from different sites during fourteen expeditions carried out from 18th October 2022 to 19th December 2022. From each sampling site, a square meter area was delimited and a composite soil sample was prepared by combining four subsamples, with each of them approximately 0.5 m apart from the others. A core of 5 cm of height and 5 cm of diameter was employed to collect the topsoil subsamples.

Once at the laboratory, each sample was homogenized and separated into two portions. On the one hand, a part of the sample was used for the determination of its moisture and organic matter content. On the other hand, a second portion was submitted to the following sample preparation protocol to enable the posterior microplastics identification by using stereomicroscopy and micro-Fourier transform infrared spectroscopy: i) a digestion process to remove the organic matter of the soil matrix with H_2O_2 at 60 ºC for 2 h; ii) a flotation step to achieve a density separation of the microplastics (using an aqueous saturated NaCl solution); and iii) a vacuum-assisted filtration to carefully retain the microplastics present in the supernatant on metallic filters of 50 µm. The second and third steps were repeated four times in total. In all the cases, the analyses were performed in triplicate.

The described protocol allowed for the first time the determination of microplastics in soils from a European National Park, and resultant data is presented herein in terms of concentration, shape, size, color and chemical composition of the found microplastics.

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YP-18

Integrating coated blades into environmental samplers: On-site extraction and direct mass spectrometric determination of emerging organic pollutants

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Keywords: *On-site extraction, Emerging organic pollutants, Coated blade spray, Ambient ionization, Mass spectrometry*

In this communication, the on-site extraction of emerging organic pollutants (benzophenones, estrogens, phytoestrogens and triazines) was carried out using coated blades as extractant phase. The coated blades were integrated in a sampling device which combines the extraction and preconcentration of the analytes. The sampler was designed using an alligator grip attached to a little engine by means of a screw. This engine stirs the sample improving the diffusion of the analytes to the coated blade. The use of the alligator grip permits the easy attachment/detachment of the coated blades from the sampler. Furthermore, the coated blades simplify the analytical procedure thanks to its direct coupling with mass spectrometry. In coated blade spray (CBS), the electrospray, which contains the analytes, is generated by the application of a high voltage (5.5 kV) to the substrate. Ambient ionization mass spectrometry (AIMS) is an alternative to the classical mass spectrometry analysis, which permits the direct introduction of the analytes into the inlet of the mass spectrometer.
To demonstrate the potential of this coupling for determining emerging organic pollutants, the variables affecting the on-site sampling/extraction process (pH, ionic strength, and extraction time) were firstly evaluated. Finally, under the optimized conditions, the methodology was validated by CBS-MS. In order to increase the potential of this application, the sequential elution of both sides of the materials was carried out. This approach permits the simultaneous determination of analytes that are ionized in positive (benzophenones, estrogens and triazines) and negative (phytoestrogens) ionization modes.

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YP-19

Determination of microplastics in a membrane bioreactor-based wastewater treatment plant

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Keywords: *Microplastics, Wastewater treatment plant, Membrane bioreactor, Ultrafiltration membranes*

In the year 2021, the annual production of plastics reached approximately 390 Mt, being the packaging sector the largest consumer of plastics worldwide (44%) [PlasticEurope, 2021]. This figure reflects the important role that plastics play in daily live, but also the enormous environmental problem they generate when used irrationally and when their management is inadequate. The problem is further aggravated when they fragment into sizes as small as 1 µm-5 mm (largest dimension), which are known as microplastics. Currently, wastewater treatment plants (WWTPs) play a significant role in the presence of microplastics in the environment, acting as both source and sink for microplastics, which is why they are the subject of numerous investigations.
Membrane bioreactors (MBRs) have emerged in recent years as an interesting and breaking technology for the advanced treatment/regeneration of domestic wastewater. In this regard, the new facilities to be implemented and operated on the island of Tenerife (Canary Islands, Spain), and also in different places around the world, will mostly apply this process, where the conventional secondary clarifier with activated sludge is replaced by ultrafiltration membranes. MBRs have shown to retain an important amount of microplastics, playing a very important role in the prevention of microplastics release where recycled wastewater is used [Chemosphere 238 (2020) 124593].
In this study, the presence and characterization of microplastics at different points of a domestic WWTP operated by MBR technology, has been developed. For this purpose, the organic matter was digested with H_2O_2 33% w/v for two hours. After filtration through stainless steel filters, microplastics were visualized under a stereomicroscope and the composition determined by micro-Fourier transform infrared spectroscopy. Besides, the most relevant physico-chemical parameters were also determined in order to study possible correlations between them and the presence of microplastics.

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YP-20

Cymodocea nodosa seagrass meadow as microplastics sink: Description and quantification

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Keywords: *Cymodocea nodosa, Marine sediments, Microplastics, Canary Islands, Micro-Fourier transform infrared spectroscopy*

Cymodocea nodosa seagrass meadows are one of the most important marine ecosystems of the sandy seabed of the Canary Islands, providing several ecological services, such as primary production, habitats, nurseries and coastal protection [BIOGES, Universidad de Las Palmas de Gran Canaria, 68 pp.]. Nowadays, it is known that marine sediments can act as a source and sink of microplastics and the same phenomenon is also occurring in seagrass meadows, mainly because seagrass leaves can be trapping plastic particles from the water column favoring their burial and accumulation into the sediment.
In this work, the microplastics content of two *Cymodocea nodosa* seagrass meadows sediments from the Canary Islands (El Médano in Tenerife and Playa del Inglés in Gran Canaria) were studied. Samples of marine sediments were collected by scuba divers using stainless-steel corers of 10 cm long and 5 cm diameter. In each meadow, four habitats were sampled: (1) dense seagrass meadow sediment, (2) adjacent unvegetated sediment, (3) lax seagrass meadow sediment, and (4) adjacent unvegetated sediment. Nine samples were taken in each habitat. Stainless-steel corers were transferred to the laboratory and refrigerated until processing.
For sample preparation, the first 5 cm of the surface sediment was taken from each corer and digested with H_2O_2 at 60 °C for 2 hours followed by a flotation process with saturated NaCl solution. The solution was left for an hour and filtrated under vacuum through a 50 µm stainless-steel filter. The flotation procedure was repeated 4 times and each filter was visualized under a stereomicroscope [Chemosphere 288 (2022) 132530]. Results show a higher abundance of microplastics in the dense sediment of both seagrass meadows and in the adjacent unvegetated sediment of the lax seagrass meadows. Around 98% of the microplastics found were fibers, mainly transparent (83%) and blue (11%) being the most common size between 1 and 2 mm (35.1%), followed by 0–1 mm (34.1%). Based on these results, it could be concluded that *Cymodocea nodosa* seagrasses could be acting as a sink for microplastics. The composition of a subset of particles was determined by micro-Fourier transform infrared spectroscopy.

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YP-21

Determination of microplastics in three species of sea urchins (*Paracentrotus lividus*, *Arbacia lixula* and *Diadema africanum*) from different coastal localities of Tenerife and La Palma (Canary Islands, Spain)

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Keywords: *Sea urchin, Extraction, Microplastics, Canary Islands, Micro-Fourier transform infrared spectroscopy*

Sea urchins play an important role in the structure of coastal benthic communities [Mar. Environ. Res. 66 (2008) 259–270], being also affected by contaminants like microplastics. In fact, the presence of submarine outfalls and land runoffs, which represent an important source of these pollutants in the vicinity of the coasts, makes these organisms susceptible to microplastic contamination due to their coastal habitat and mode of feeding (grazing action).
In this work, sea urchins of three different species (*Paracentrotus lividus*, *Arbacia lixula* and *Diadema africanum*), were collected by scuba divers in different localities on the islands of La Palma and Tenerife (Canary Islands, Spain) at a depth between 3 to 11 meters, between 2020 and 2022. Once at the laboratory, samples were frozen until their analysis.
The sea urchins were thawed at room temperature and later the digestive tracts and gonads were separated and digested with 33% w/v H_2O_2 at 60 °C for 48/24 hours (depending on the specie). After that, each digested sample was filtered through a 50 µm stainless-steel filter to separate microplastics from the digested matrix and each filter was visualized under a stereomicroscope. Each tentative microplastic found was classified according to its shape, size and color [Environ. Sci. Technol. 46 (2012) 3060–3075]. Results revealed a similarity in the distribution pattern among the three sea urchin species, independently of the sampling location, finding in all species mainly transparent fibers with an average size between 500 and 750 µm. The composition of a subset of particles was determined by micro-Fourier transform infrared spectroscopy. Most of the particles found had a cellulosic composition (natural and semisynthetic), though an important concentration of synthetic fibers were also found.

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YP-22

Ultrasound-assisted extraction followed by liquid chromatography and tandem mass spectrometry for the simultaneous determination of 9 herbicides in soil

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Keywords: *Herbicides, Ultrasound-assisted extraction, Liquid chromatography-tandem mass spectrometry, Sample preparation, Soil*

Due to the huge demand for agri-food products for the world population's sustainability, some alternatives such as the use of herbicides have been arising to improve their production. Herbicides are chemical products that inhibit or remove unwanted plants in crops, benefiting the crop's growth and making its recollection easier. Nevertheless, herbicides can be harmful and show adverse effects on health (e.g. carcinogenicity, mutagenicity, reproductive toxicity, etc.) and the environment (e.g. toxic to aquatic life with long lasting effects) [Water Environ. Res. 91 (2019) 1009–1024]. A new alternative that allows reducing the necessary dose of these herbicides as well as the environmental impact is the use of amendments based on biochar whose main purpose is the carbon sequestration which has a positive impact in crops' fertility and growth [Agronomy 9 (2019) 588].
The aim of this work is the development of an analytical methodology based on ultrasound-assisted extraction (UAE) followed by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) for the identification and quantification of 9 herbicides in soil samples. Preliminary experiments (extraction technique, solvent extraction and herbicide recovery comparison in soil with and without organic amendment) have been carried out. Then, the most critical parameters affecting UAE (percentage of methanol in the extraction solvent, extraction time, amount of soil sample and extraction solvent volume) were optimized by design of experiments. Furthermore, UAE and microwave-assisted extraction (MAE) performance were compared as well as the influence of the extraction temperature. Under the optimum conditions, the UAE-LC-MS/MS method was validated and extended to other herbicides showing satisfactory results in terms of linearity ($R^2 \geq 0.9912$) and accuracy obtaining quantitative recoveries (75-123%) and precision (RSD between 3-10% in almost all cases). Finally, the simple, green, fast and low cost developed method was applied to real contaminated soil samples from Galicia, revealing the presence of 7 out of the 9 studied herbicides with S-metolachlor high concentrations in all samples.

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YP-23

Quantification of volatile methylsiloxanes in water samples using liquid-liquid extraction assisted by sonication and GC-MS

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Keywords: *Volatile methylsiloxanes, River water, Seawater, Liquid-liquid extraction, Gas chromatography-mass spectrometry*

Volatile methylsiloxanes (VMSs) are synthetic chemicals characterized by their low molecular weight and high volatility. These compounds are intensely produced worldwide and commonly used in various industrial and consumer applications (personal care products, cosmetics, antifoaming agents, lubricants, electrical insulators, etc). Recently, VMSs have been the subject of environmental and health concerns. The main issue is their potential persistence and bioaccumulation in the environment. Once released into the air or water, these compounds can undergo long-range transport, leading to their presence in remote regions. They are also known to bioaccumulate in aquatic organisms, raising concerns about their potential impacts on ecosystems.
In this sense, the aim of this work is to determine the presence of VMSs in river and sea water samples, where monitoring their levels is important to assess potential environmental impacts and help define potential regulatory guidelines. Thus, seven VMSs (D3, D4, D5, D6, L3, L4 and L5) were quantified by gas chromatography-mass spectrometry (GC-MS) using a liquid-liquid extraction assisted by sonication to ensure a low consumption of organic solvents. Due to matrix effects, the quantification of seawater samples was performed using a matrix-matched calibration. In total, 34 river (from four impacted rivers in the North of Portugal) and 91 sea (from Portugal and Spain) water samples were analyzed and the levels of total VMSs ranged from n.d. to tens of $\mu g \cdot L^{-1}$ in both matrices.

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YP-24

Assessing the potentialities of an easy-to-use sample treatment strategy: Multivariate investigation on "Moka extraction" of typical ingredients from dietary supplements

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Keywords: *Moka pot, Dietary supplements, Fractional factorial design, Highly polar compounds*

Since its invention in 1933 by Mr. Bialetti, Moka has diffused worldwide as one of the most common methods to prepare Italian coffee. Moka's success is due to its peculiar configuration, which allows to extract the powdered coffee with higher pressure, temperature and speed, achieving good extraction efficiencies for caffeine and other flavoring and aromatic substances, generally associated with coffee's quality and its characteristics. Moka's functioning principle is somehow similar to that of accelerated solvent extraction (ASE) technique, a common sample preparation strategy, which requires complex and expensive instrumentation. Herein, a possible application of a cheap and easy-to-use Moka pot has been explored as sample preparation procedure. Several polar analytes, including methylxanthines, sweeteners, and taurine, which are typical ingredients of dietary supplements (DS) for athletes, were considered and extracted from commercial products. Since these compounds are very polar ($logD_{(pH=7)}$ from -2.6 to -0.5) and present ionizable functions, the selected chromatographic separation was hydrophilic interaction liquid chromatography (HILIC), which was previously optimized through a two-step design of experiments (DoE), coupled with tandem mass spectrometry (MS) as detection system.
Four different pre-workout DS were bought online and were pooled to obtain a general matrix, containing all the selected analytes, to be used for subsequent Moka extraction optimization. As a first step, a 2^{4-1} fractional factorial DoE was set to investigate the effect of four experimental variables on the extraction efficiency of the analytes, thus performing 8 experiments plus a center point. The investigated variables included heating temperature (125-175 °C), solvent pH (4-9), percentage of organic modifier – acetonitrile, ACN – within the extraction solvent (0-15%) and amount of sample to be extracted (0.5-1.5 g). Since the method aimed to use a low sample mass, silica was employed as inert filler to reach a total amount of 6 g (therefore ranging 5.5-4.5 g) to guarantee an uniform distribution within the Moka's funnel filter. By contrast, the total amount of extraction solvent was fixed at 40 mL, since Moka works properly only if properly filled. Furthermore, also the heating time was fixed (10 minutes), since preliminary tests showed that this variable is critical to achieve satisfactory repeatability. The obtained extracts were allowed to reach room temperature and transferred in a 50 mL volumetric flask, adjusting the volume by adding water. Finally, a small amount of each extract was filtered and properly diluted prior to HILIC-MS/MS analysis.
Chromatographic peak areas (normalized for the actual amount of sample extracted in each experiment) were used as responses and elaborated through the Chemometric Agile Tool software [R. Leardi et al., (2023) http://gruppochemiometria.it/index.php/software]. First, a principal component analysis (PCA) was performed on autoscaled data, highlighting that most of the variance was explained by the first PCs (77.7% and 15.3% for PC1 and PC2, respectively). While the analytes heterogeneously distributed along PC2, they presented similar and positive loadings on PC1, suggesting that increasing PC1 means maximizing the extraction efficiencies. Hence, a regression model was computed using the PC1 scores as unique response, instead of modelling single peak areas. It is worth noting that the specific DoE used implies that some of the effects of the variable interactions are confounded. Assuming that three-terms interactions are expected to be not significant, the obtained model showed that the most relevant variable is the mass of sample, with a negative coefficient. This suggests that either the fixed volume of extraction solvent or the extraction times may be not enough to extensively extract a higher amount of sample within the Moka. Moreover, both heating temperature and percentage of ACN presented a positive – even if small – effect in increasing the extraction efficiency, while solvent pH resulted non significant. The interaction coefficients are less easily interpretable, since their effect are confounded by the model. In fact, one coefficient resulted significant with a small negative effect, but it was not possible to discern the partial contributions of the two aliased interactions (temperature – organic modifier and solvent pH – mass of sample interactions). These first considerations will be useful to find the optimal method prior to validation and application to single DS. Quantitation results could be compared with other more classical methods. For example, in our lab a salt-assisted liquid-liquid extraction (SALLE) was previously developed, since salts are useful to extract polar organic compounds from aqueous phases. The remaining amounts of salts within the organic layer, can interfere with the analysis. Moka extraction avoids the use of salts but it consumes more sample and solvents than SALLE, even though the smallest available Moka was employed. In conclusion, Moka extraction applied to DS is promising, thanks to its cost-effectiveness and easiness. Further studies are planned to reduce the operational quantities and to extend the possible analytes to be searched and matrices to be processed.

YP-25

DUT-52 metal-organic framework as sorbent for contaminants of emerging concern in micro-dispersive solid-phase extraction: Pros and cons

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Keywords: *Metal-organic frameworks, Micro-dispersive solid-phase extraction, Contaminants of emerging concern, Environmental analysis*

Water contamination is one of the biggest issues worldwide. In this sense, water quality monitoring is the unique way to assay the conditions and the presence of negative substances in environmental waters; to ensure proper human health and for the good state of natural ecosystems.
Contaminants of emerging concern (CECs) are a group of organic compounds that have been widely studied due to their endocrine disruptor effects in human and animal health. Compounds like parabens, present in several personal care products, bisphenols, present in plastics, and benzophenones, as ultraviolet filters, are examples of these kinds of contaminants and have been detected in environmental waters. However, CECs and other organic contaminants are difficult to determine in waters because they are present at very low concentration, being necessary highly sensitive analytical methods for their determination. To achieve proper monitoring of CECs, sample preparation is clearly required.
New trends in extraction technologies involve, among other strategies, minimizing as much as possible the amount of sorbent materials and the usage of a small volume of toxic organic solvents, thus developing micro-scale procedures. An example is micro-dispersive solid-phase extraction (μ-dSPE), in which the extraction sorbent is directly dispersed in the sample solution, this way producing a more efficient interaction with analytes and, thus, providing higher extraction performance than the static mode of μ-SPE.
The selection of the sorbent material incorporated to a μ-dSPE method is one of the most important variables to study. Metal-organic frameworks (MOFs) are a group of novel materials formed by metallic clusters and organic ligands linked by coordination bonds, presenting outstanding properties for analytical proposes such as ultra-low densities, permanent porosity, accessible cages, tunnels and modifiable pores, and the highest surface areas known. DUT-52(Zr) is a useful MOF for microextraction, given its low toxicity, stability, easy synthesis, and adaptability to incorporation in different microextraction procedures.
The objective of this study is to develop a fully optimized μ-dSPE-DUT-52(Zr) method in combination with UHPLC-MS/MS for the monitorization of CECs in environmental waters.

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YP-26

Green and effective procedures of biological samples preparation for the determination of psychoactive substances

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Keywords: *Biological samples, Extraction procedures, Green chemistry, Psychoactive substances*

The preparation of the sample for analysis is the most important stage of the entire analytical procedure, which affects the reliability of the results obtained in the subsequent stages of the determination. It is particularly important in the context of the analysis of samples with a complex matrix, such as biological samples. The use of an appropriate extraction procedure in the analysis of such samples makes it possible to isolate the target analytes from the sample matrix, furthermore allowing the preconcentration of the sample before instrumental analysis. Currently, developed extraction procedures are subject to many requirements in order to ensure the selectivity and efficiency of the extraction process while paying attention to the greenness and safety of the procedure. This work presents examples of optimization and application of selected extraction procedures that can be used in the analysis of biological material containing selected psychoactive substances. The developed methods are based on the analysis of, among others, samples taken with the dried blood spot (DBS) method, the use of solid-phase microextraction with commercially available sorbents, and the use of cheap and ecological sorbent materials produced in a laboratory. These procedures have been developed taking into account aspects such as the availability of a small amount of sample for analysis, limiting the use of hazardous and toxic solvents, and the price and time of sample analysis. The developed methods can be successfully used in the analysis of biological samples in order to isolate a wide range of psychoactive substances for the purposes of toxicological analyses. In addition, the presented studies tested the possibility of using electrochemical detection with the application of inexpensive screen-printed electrodes in the analysis of extracts from biological samples previously subjected to extraction procedures. The use of electrochemical detection in the analysis of extracts from biological samples may contribute to reducing the use of energy-intensive equipment, such as a mass spectrometer, thus can make the method more economical and environmentally friendly.

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YP-27

An emerging extraction technique based on micro-solid-phase extraction followed by GC-MS analysis for quantification of opium alkaloids in poppy seed infusion

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Keywords: *Opium alkaloids, Poppy seed infusion, µSPEed, Gas chromatography-mass spectrometry, Food safety*

Poppy seeds are used for the preparation of relaxing infusions for insomnia and anxiety. This is due to their opium alkaloid content due to contamination with latex from the plant itself (*Papaver somniferum* L.). However, the lack of knowledge of the concentration in infusions and uncontrolled use has led to cases of intoxication. To avoid this, there is a maximum limit of morphine equivalent (morphine + 0.2 × codeine) in the seeds of 20 mg/kg. So, it is necessary to ensure that this is being complied with. In addition, health authorities are demanding further studies with other opium alkaloids (OAs) such as thebaine, papaverine and noscapine, as they can also be found in high concentrations and maybe even more toxic. Therefore, the aim of the present work was to develop, optimise and validate an effective analytical methodology to quantify five OAs in poppy seed infusions. This method is based on a micro-solid-phase extraction (µSPEed®) followed by gas chromatography analysis coupled to a mass spectrometry detection system (GC-MS). Firstly, for the optimization of the µSPEed® procedure, nine cartridges with different chemical structures (six silica-based: C_4, C_8, C_{18}, silica, APS (WAX, weak anion exchanger), PFAs (50% WAX, 50% C_{18}) and three polymeric-based: PS/DVB-RP (reversed phase), PS/DVB-SCX (strong cation exchanger) and PS/DVB-SAX (strong anion exchanger)) were evaluated. Besides, other parameters of the procedure were optimised, such as the pH, number of cycles, and the nature of elution solvent. As a result, it was obtained that this technique was able to eliminate possible matrix effects and concentrate the extract 10 times, achieving lower detection limits. Once the methodology had been optimised, a successful validation was carried out in terms of linearity, detection and quantification limits, matrix effect, precision, accuracy, and selectivity. Therefore, the method was applied to quantify four infusions made with different seeds to know the concentrations that can be found in homemade infusions with commercially available poppy seeds. The infusion conditions used were 95 ºC for 5 min, as these are the most common. The five OAs studied were quantified in all the samples and even one of them showed a high amount of morphine (1563 µg/L). This high concentration indicated that the seeds used had a concentration twice the maximum limit legislated by the EU (20 mg/kg) and highlighted the need to warn the population of this dangerous practice.

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YP-28

Multiplex extraction of four emerging contaminant families through 3D-printed stir-towers incorporating metal-organic frameworks

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Keywords: *Solid-phase extraction, Emerging contaminants, 3D-printing, Metal-organic frameworks*

The analysis of emerging pollutants plays a vital role in environmental monitoring and safeguarding human health. These pollutants encompass a diverse range of contaminants, including pharmaceuticals, personal care products, and industrial chemicals, among others, which have the potential to adversely impact ecosystems and human well-being. Traditional monitoring methods often fall short in detecting and quantifying these emerging pollutants due to their unique properties and low concentrations in the environment. Therefore, the development of sensitive and reliable analytical techniques, specially focused on sample preparation, is crucial to identify and assess the presence of these emerging pollutants. In this regard, 3D-printing technologies have gained notoriety recently thanks to its capability to provide a way to cheaply and quickly design and engineer prototypes in the lab. This technology appears to be particularly useful in Analytical Chemistry, specially in the field of sample preparation, as 3D-printing can provide tailored structures that can be easily adapted to different and novel modes of solid-phase extraction. However, even if the customized 3D-printed devices are used, the low surface area and limited selectivity mitigates their use in sample preparation. To overcome these limitations, 3D-printed structures can hold advanced functional materials to obtain composite devices with enhanced features to carry out the extraction. Hence, advanced functional materials, such as metal-organic frameworks (MOFs), provide a charming alternative to be combined with 3D-printing to obtain fine-tuned devices with increased extraction capabilities. In addition, the possibility to use different MOFs offers the opportunity to increase the selectivity for different pollutants families, providing all-in-one extraction systems.

In this work, tower-shaped devices with multiple holes have been meticulously designed to incorporate various MOFs. However, the attachment of the MOF to the different holes is not possible in the absence of a previously laser-assisted polymerization of a glycidyl methacrylate-based polymer. This innovative design allows the use of up to 4 different MOFs, enabling a high degree of customization. In this case, the prepared devices have been coated with MOF-801(Ce), MIL-100(Fe), ZIF-8(Zn) and ZIF-67(Co). The devices were employed to extract twelve analytes simultaneous, belonging to four different families of emerging contaminants: tetracyclines, non-steroidal anti-inflammatory drugs, parabens and aromatic phenols from water samples. The findings revealed remarkable extraction capacities and enhanced selectivity, as each contaminant family exhibited greater affinity towards specific MOFs. Consequently, this novel approach, which combines 3D-printed devices with MOFs, paves the way for the development of multiplex extraction systems, offering a versatile and highly efficient solution for the simultaneous extraction of diverse analytes from complex matrices.

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YP-29

Perovskites: New extraction materials with luminescent properties for preconcentration and sensing of emerging pollutants

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Keywords: *Perovskite, Quenching, Fluorescence, 2,4-Dinitrophenol, Extraction sensors*

Emerging contaminants are compounds that have recently been detected in the environment and may have a significant threat to both the ecosystems and human health. However, the low concentrations of these substances in nature often make it challenging to accurately quantify these substances using conventional detection methods. Therefore, there is of great interest to develop analytical methodologies capable of detecting and monitoring these emerging pollutants, in order to prevent potential environmental consequences. One such emerging contaminant is 2,4-dinitrophenol (2,4-DNP), which has been widely used as a non-selective pesticide, due to its role as a uncoupler of the electron transport chain. This property of 2,4-DNP poses an inherent risk to all living organisms. Therefore, development of affordable, rapid, simple and sensitive analytical methodologies to determine 2,4-DNP is of utmost importance. A recent trend in analytical chemistry has been the exploration of novel sensing materials that can generate a signal in the presence of certain analytes. Perovskites (PKs) are a class of crystalline materials that shows fluorescent properties, which intensity changes in presence of other compounds due to effects such as quenching or antenna. However, PKs are generally unstable in water, seriously limiting its utility as sensing materials.

This work has focused on the exploration of water-stable hybrid PKs, composed of lead and methylamine, to be used not only as a fluorescence sensor for detecting 2,4-DNP in dispersive mode, but also as a preconcentrating agent. With this goal in mind, optimization of the synthesis, characterization of the materials, optimization of the sensing and the extraction procedures was carried out. The results demonstrate that the water-stable synthetized PKs exhibit strong fluorescence, enabling low detection limits and complete recovery of the analytes even at large loading volumes. In this regard, the capacity to load large sample volumes and preconcentrate the PKs (containing the analyte) in minute amounts of volume to perform the dispersive sensing allows high preconcentration factors. Hence, by advancing the understanding of these materials, it is possible to enhance their performance and unlock broader applications in the field of Analytical Chemistry, and more specifically in the development of novel materials with multiple enhanced features, such as extraction and sensing.

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YP-30

A dual liquid/solid-phase microextraction system using carbon nanotubes for cadmium extraction from water samples

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Keywords: *Cadmium, Carbon nanotubes, Hollow fibers, Dual liquid/solid microextraction, B*is(2-ethylhexyl) phosphoric acid

Monitoring of metals in natural waters continues being a challenge for analytical chemistry due to the complexity of the matrix and their extremely low concentration levels. Therefore, extraction techniques have been a powerful tool to isolate and pre-concentrate the analytes prior to the instrumental analysis. Among them, the most commonly used for metal analysis are both solid- and liquid-phase extractions, especially in their miniaturized versions solid-phase microextraction (SPME) and liquid-phase microextraction (LPME). Each of them exhibit both advantages and disadvantages.

In SPME, the key factor is related with the selection of the adsorbent material according to the characteristics of the analyte. Nowadays, carbon nanotubes (CNTs) appear as a versatile material to extract metals from water thanks to their high adsorption capacity towards these elements. Besides, CNTs surface can be modified by the addition of functional groups, such as -OH and –COOH, to improve the metal extraction capacity since ionic exchange can take place in addition to physical adsorption.

In the case of LPME, hollow-fiber liquid-phase microextraction (HF-LPME) combines the use of very low volumes of organic solvents and high stability of the system thanks to the use of a polypropylene porous fiber as a support for the organic phase used for the extraction. Nevertheless, the diffusion of analytes from the sample to the receiving solution is the limiting step and high extraction times are sometimes required to achieved high enrichment factors. So, different alternatives have been used to accelerate the transport of analytes, as the application of an electric potential or the combined use of a liquid extractant and a solid adsorbent (dual extraction). Although this last alternative has been successfully applied to the extraction of organic compounds, the application to the extraction of metals is still very limited.

Then, this work explores the synergistic effect on the extraction efficiency when CNTs are used joint to the organic extractant bis(2-ethylhexyl) phosphoric acid (D2EHPA) in a HF-LPME system to extract cadmium from aqueous solutions. To do that, a two phases configuration was used, with the pores and the lumen of the fiber filled with the organic phase.

Liquid-liquid extraction experiments have shown a synergetic effect between D2EHPA and CNTs functionalized with –COOH to extract relative high cadmium concentrations (0.5 $mg \cdot L^{-1}$). Then, preliminary experiments with different sizes of hollow fiber were performed maintaining the same chemical conditions. In addition, application of this system to real cadmium concentrations in waters was also tested (0.5-1 $\mu g \cdot L^{-1}$). In order to established the synergetic effects, each experiment was performed only with CNTs or D2EHPA in the organic phase as well as with the presence of both extractants simultaneously.

Once the efficiency of the HF-LPME system was proved for low cadmium concentrations, a univariate optimization was performed to get the maximum enrichment factor. The variables to be considered during optimization were D2EHPA and CNTs concentrations in the organic phases, the stirring rate and the extraction time. Finally, the recovery of the cadmium extracted with an acidic solution was also tested in order to evaluate the applicability of the optimized system in a three phases configuration.

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YP-31

Determination of lysozyme in foods using aptamer-based hybrid affinity monolith in paper-based devices

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Keywords: *Allergenic egg protein, Aptamer, Lysozyme, Paper-based devices, Polymer-bound aptamer*

Egg allergy is one of the most common food allergies in infants. Ovomucoid, ovalbumin, ovotransferrin, lysozyme and α-livetin are the 5 most important egg allergens. Specifically, lysozyme is a glycoside hydrolase that represents 3.5% of the proteins present in egg white. To guarantee consumer's safety, it is essential to establish accurate and sensitive detection and quantification methods for allergenic proteins. Aptamers have been recognized as innovative and stable recognition ligands, demonstrating their usefulness in diverse analytical applications. Particularly notable is their ability to isolate small molecules and biomacromolecules, including proteins. Therefore, its combination with different supports, such as paper substrates, presents several benefits. In particular, paper acts as a low-cost support platform to anchor for example an aptamer-modified polymer, which will provide a high selectivity for the target molecule.
In this work, paper-based devices coated with an aptamer-modified polymer were prepared to selectively isolate the allergenic egg protein lysozyme from different foodstuffs. To this end, a piece of paper has been coated with an aptamer-based polyhedral oligomeric silsesquioxane (POSS)-containing hybrid affinity monolith prepared via a "one-pot" process, which was carried out using a UV laser pointer. Polymerization parameters were adjusted in order to obtain a stable and homogeneous layer of aptamer modified-monolith onto the piece of paper. Next, different experimental conditions (such as loading and elution solvents, extraction and desorption temperature and time, loading capacity and breakthrough volume) were investigated. Under the optimal conditions, the developed paper-based devices were applied to different foodstuffs susceptible of containing non-declared egg allergens.

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YP-32

Aptamer-modified elastic 3D-printed springs for enhanced extraction of lactoferrin in food samples

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Keywords: *Aptamer, Solid-phase extraction, Lactoferrin, 3D-printing, Allergenic proteins*

Several proteins of cow's milk induce allergenic reactions in infants at the first years of life, being casein fraction, β-lactoglobulin and α-lactalbumin the major allergens. However, other proteins present in very low quantities, such as serum albumin, immunoglobulins, and especially lactoferrin (LF), may also be important allergens. The symptoms produced by LF exhibit a wide spectrum, ranging from minor to moderate or severe occurrences, impacting the skin, respiratory system, digestive system, or even anaphylactic shock. Hence, the development of analytical methodologies able to extract LF holds significant importance in ensuring food safety by accurately detecting and confirming the presence or absence of LF.

In this regard, the use of 3D-printing presents a promising opportunity for the development of innovative devices tailored for sample preparation of allergenic proteins. The inherent advantages of 3D-printing, including high layer precision, wide range of available materials and chemical resistance, among others, make it a promising technology in this field. However, the selectivity and surface area of these printed devices is limited; therefore, its combination with advanced functional materials is necessary. Hence, an intriguing solution lies in the incorporation of aptamers, which are single-stranded nucleic acid molecules, either RNA or DNA, which bind a specific target molecule, or family of target molecules. These DNA oligomers are highly stable, reusable, exhibit high activity and can be easily attached to the surface of other devices.

In this work, an elastic 3D-printed device was designed and printed to enable easy compression and expansion. This unique feature allows for its convenient use within a simple syringe, facilitating the performance of the different steps of extraction and maximizing the preconcentration factor. In order to obtain a highly selective 3D-printed device, the surface of this spring system was modified with a LF-specific aptamer by covalent attachment. In addition, investigations were conducted to characterize the surface modification of thesupport, and thus enhancing the LF extraction efficiency. These efforts aimed to establish an analytical methodology for the extraction of LF from food samples. The system provided remarkable loading capacities and achieved substantial preconcentration factors. The results demonstrated the exceptional capabilities of combining elastic 3D-printed devices with selective aptamers offering a powerful and efficient approach for the extraction of LF.

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YP-33

Sustainable 3D-printed devices modified with aluminium-based metal-organic frameworks for extraction of picolinic herbicides from environmental waters

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Keywords: *Picolinic herbicides, 3D-printing, Sustainable materials, Metal-organic framework, Solid-phase extraction*

Picolinic herbicides are a class of herbicides used to control the growth of weeds or unwanted plants in agricultural crops, gardens, and green spaces. These herbicides contain chemical compounds based on picolinic acid (PA), which is a synthetic substance similar to few acids found naturally in some plants. Picolinic herbicides are effective in inhibiting the growth of weeds by interfering with protein synthesis and cell division in target plants. This results in the inhibition of weed growth and, eventually, their death. However, picolinic herbicides, characterized by their high persistence and ability to bioaccumulate in the environment, pose a potential risk to human health and can cause toxicity in aquatic life. Additionally, their prolonged use can result in contamination of groundwater and the development of weed resistance. Then, there is a need to develop accurate and efficient analytical methodologies for detecting and quantifying PAs in environmental waters.

In this regard, the use of advanced functional materials, such as metal-organic frameworks (MOFs) are a ground-breaking approach in the development of innovative methodologies for extracting PAs from environmental waters. Despite the well-known advantages of MOFs (such as high surface area, high thermal and chemical stability, tailorable functionalization, among others), its direct use as sorbents is limited due to difficulties in shaping and handling these crystalline powders. Hence, the combination of these materials with sustainable supports, such as those produced by the layer-by-layer manufacturing technique known as 3D-printing, which is an innovative technique to develop novel devices that act as supports for advanced functional materials. Among the large number of modalities in 3D-printing, fused deposition modelling (FDM), based on a heated thermoplastic material filament onto a platform to create a 3D-object, stands out as one of the most widely used techniques. The popularity of these devices arises from the wide array of materials, including sustainable options, that are readily available, as well as the ability to efficiently manufacture customized devices. Therefore, the preparation of composite devices based on 3D-printing and MOFs provides a new class of materials that can be readily applied across various fields.

In this study, an aluminium-based MOF has been synthesized onto sustainable 3D-printed structures to be used as extraction devices of PAs from environmental waters followed their analysis by HPLC. For this purpose, thermoplastic based on polylactic acid doped with pine tree residues, as sustainable material, was used to print the 3D-printed parts. Then, the surface modification of this part was investigated in detail in order to incorporate the aluminium-based MOF as well as to maximize the amount of MOF located onto the 3D-printed surface. The resulting 3D-printed devices, containing the MOF, were characterized by infrared spectroscopy and scanning electron microscopy and used for the extraction of PAs. Various parameters that affect the extraction efficiency (extraction time and temperature, eluent solution and volume, among others) were studied. The designed composite constructed by integrating 3D-printed components with MOFs demonstrated exceptional extraction capabilities for various PAs. These results underscore the extensive possibilities offered by this fruitful combination, thus constituting affordable and sustainable methodologies aimed at analyzing emerging pollutants.

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YP-34

Enhanced extraction of sulfonamides from environmental waters using sustainable 3D-printed devices coated with ZIF-8

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Keywords: *Sulfonamides, 3D-printing, Sustainable materials, Metal-organic framework, Solid-phase extraction*

Sulfonamides (SAs) are widely used pharmaceuticals in human and veterinary medicine for the treatment of systemic infectious diseases. However, due to the poor assimilation of these substances in the human body, these compounds are excreted into the environment through urine or feces, either as parent compounds or metabolites. Consequently, SAs are classified as emerging or "pseudo-persistent" pollutants, characterized by its constant presence in the ecosystem and limited biodegradability. This fact constitutes a potential threat to human health, since it can contribute to the development of antibiotic-resistant bacteria, with detrimental consequences. Hence, the development of accurate and reliable analytical methodologies for the detection and quantification of SAs in environmental waters is mandatory. Additionally, it is highly desirable to enhance the features of these methodologies by developing adsorbents as remediation systems for the efficient removal of these compounds in wastewater.

In this regard, 3D-printing emerges as an innovative strategy for developing novel devices designed for the extraction of SAs from environmental waters. Among the large number of modalities in 3D-printing, fused deposition modelling (FDM) stands out as one of the most widely used techniques. FDM involves the layer-by-layer deposition of a heated thermoplastic material filament onto a platform to create a 3D-object. This popularity stems from the extensive range of available materials, including sustainable ones, and the ability to swiftly produce tailored devices. However, a drawback of these 3D-printed devices is their limited surface area, needing its combination with other advanced functional materials, such as metal-organic frameworks (MOFs). Thus, MOFs can provide to these 3D-printed structures the adequate features to enhance their extraction capabilities.

In this study, an attachment of ZIF-8 MOF to square-shaped 3D-printed parts was investigated. First, a sustainable thermoplastic based on polylactic acid doped with pine tree residues was used to print the 3D-objects. Next, the surface of these 3D-printed devices was modified with various reagents in order to the attachment of a ZIF-8 prepared by a green synthesis. The obtained 3D-printed composite part was applied to the extraction of SAs from environmental waters, followed high-performance liquid chromatography analysis. The developed composite exhibited remarkable extraction capabilities for different SAs. These findings highlight the attractive combination of sustainable 3D-printing and green synthesis of MOF in the development of novel Green Analytical Chemistry methodologies for the analysis of emerging pollutants.

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YP-35

Extraction and characterization of microRNA from food wastes and seaweeds: Evaluation of anti-inflammatory properties

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Keywords: *Micro-ribonucleic acid, Food waste, Seaweed, Anti-inflammatory activity, Liquid chromatography*

MicroRNAs (miRNAs) are a novel class of small RNAs (21–25 nucleotides) with signalling roles in intercellular communications and scarcely investigated in foods. They are encapsulated into exosome-like nanoparticles or extracellular vesicles. When reaching target cells or organs, microRNAs are released from nanoparticles to regulate gens [Trends Food Sci. Technol. 135 (2023) 215–233]. MicroRNAs can repress gene expression at post-transcriptional level by silencing or promoting their degradation. Recent studies have showed that dietary microRNAs may be transferred to consumers, and they may regulate mammalian gene expression [Trends Food Sci. Technol. 135 (2023) 215–233]. These discoveries have resulted in a new concept of bioactive compounds that may exert effects at metabolism and immune response levels. Consequently, the study of the presence of microRNAs in foods has become an emerging topic. On the other hand, the hyperinflammatory syndrome developed in patients with infectious microorganisms is associated with high plasma levels of pro-inflammatory cytokines [The Lancet 395 (2020) 497–506]. Current therapies for this inflammatory syndrome is limited to steroidal and non-steroidal anti-inflammatory agents. Nevertheless, natural sources can also offer anti-inflammatory compounds acting at low concentrations and showing low toxicity. Considering the potential of some food wastes and seaweeds, this work purposes to characterize and study the anti-inflammatory properties of miRNAs extracted from different food wastes (orange peel, apricot seeds, pomegranate seeds, malt rootless, brewer´s spent grain, and watermelon residue) and from two seaweeds (*Chlorella* and *Spirulina*).
Two different commercial extraction kits were employed to recover miRNAs: E.Z.N.A MicroRNA kit (Omega BIO-TEK) and mirPremier microRNA isolation kit (Sigma-Aldrich). The extraction efficiency of the two kits was compared in terms of miRNA quantity and quality (co-extraction of proteins or contamination with phenol during extraction and elution of the sample) using a nanodrop spectrophotometer. MiRNA extracts were characterized by RP-HPLC using UV detection at 260 nm and high-resolution tandem mass spectrometry in negation ionization mode. Moreover, the anti-inflammatory properties of miRNA extract at different concentrations were evaluated in murine macrophages treated with lipopolysaccharide. Results demonstrated the presence of miRNAs in all samples highlighting seaweeds. A higher extraction yield was obtained with E.N.Z.A microRNA extraction kit. Analysis of extracts by RP-HPLC required a previous optimization of the ion-pairing reagent (type and concentration), elution gradient, and temperature. Best separation was obtained using 10 mM trietylamine-acetate (TEAA) buffer at 40 °C. Some miRNA extracts also showed anti-inflammatory properties.

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YP-36

Beware of vector-borne diseases widespreading. An automated molecular diagnostic workflow to detect and differentiate them

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Keywords: *Nucleic acid extraction, Quantitative polymerase chain reaction, Vector borne diseases, Automatic workflow*

Background
Vector-borne diseases are caused by parasites, virus and bacteria transmitted by mosquitos in tropical and subtropical areas, where morbidity and mortality are especially contributed by underdeveloped socioeconomic and health system. Besides, climate change, urbanization and population mobility between countries are spreading these infections and outbreaks, as well as the possibility of viral co-infection within a single host. Unfortunately, early symptoms are similar and nonspecific (fever, headache, skin rash, muscle and join pain, and gastrointestinal symptoms). Therefore, the sensitive, specific, and rapid diagnosis of these infections, is crucial to managing the pathology and selecting the appropriate treatment, and control outbreaks. In this context, automation of nucleic acid purification in combination with molecular diagnostics (qPCR) becomes very interesting [Vector-Borne Zoonotic Dis. 17 (2017) 285–296].

Aim
The main objective of this work was to evaluate the analytical performance of the VIASURE Blood Pathogens Extraction kit within the VIASURE V-Flex automated platform for the sensible and specific detection of vector borne microorganisms in blood samples. And to ensure that the presence of several pathogens in the clinical samples (co-infections) does not affect the individual amplification by the VIASURE Real-Time qPCR detection kits.

Materials and methods
A reagent kit has been specifically designed for the isolation of pathogen nucleic acids from human serum, plasma, and blood samples. The kit performance is based on the adsorption of nucleic acids to superparamagnetic beads under chaotropic conditions, several washing steps and subsequent elution under low ionic strength conditions. This technology allows the automation of the process in robotic platforms, like the VIASURE V-Flex system. An analytical performance evaluation of this molecular workflow has been performed using negative blood samples experimentally spiked with quantified WHO reference cultures. The obtained eluates were analyzed using VIASURE Real-Time qPCR detection kits in the VIASURE V-Lab96 Cycler.
First it was evaluated the analytical sensitivity (limit of detection, LoD) and linearity of VIASURE complete molecular diagnosis workflow for Zika and *Plasmodium falciparum*. Then, it was evaluated the possible interference or cross reactivity of similar analytes to the analytical sensitivity. To do so, a study of coinfections was carried out with 79 whole blood samples and 87 serum samples spiked with different concentrations of Zika Virus, *Plasmodium falciparum*, Dengue virus, Chikungunya virus, West Nile Virus, and *Leishmania donovanii*.

Results
The limit of detection (LOD) obtained for Zika virus was 1 IU/µL in serum, plasma, and whole blood. For *Plasmodium falciparum* the LOD obtained in whole blood was 5 IU/µL. The efficiency of the complete workflow obtained from the linearity assays is as follows: Efficiency=91.85%, R^2=0.9912 for Zika in serum. Efficiency=100.35%, R^2=0.9868 for Zika in whole blood. Efficiency=97.84%, R^2=0.9953 for *Plasmodium falciparum* in whole blood.
The set of qPCR results for each of the pathogens in the different co-infected matrices show the highest values of overall agreement, sensitivity, and specificity, so the co-infection assay did not present interference in the sensitivity of the molecular diagnosis workflow. In addition, no significant Ct delay was observed between co-infected samples and those infected with the same concentration by a single pathogen.

Conclusion
It has been proven that the analytical sensitivity of this workflow is the same for different biological matrices and that qPCR is a very sensitive and specific tool to quickly detect and differentiate this type of infections.

YP-37

New molecular diagnosis workflow for antimicrobial resistance detection and timing improvement in sepsis management

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Keywords: *Nucleic acid extraction, Quantitative polymerase chain reaction, Antimicrobial resistances, Automatic workflow, External quality assessment*

Background
Rapid detection of pathogens and antimicrobial resistances (AR) causing sepsis is crucial to enable an adequate and timely therapy. The gold standard method remains blood culture despite its slowness (>5 days) and complexity [Clin. Microbiol. Rev. 31 (2018) e00089–17]. The availability of qPCR: sensitive, specific, fast, automatable, and multi-target, could be a useful tool to anticipate results and optimize antibiotic therapy [Expert Rev. Mol. Diagn. 15 (2015) 681–692]. Although sepsis is an especially urgent situation, the fast detection of AR is highly important in other infectious diseases.
To achieve reliable qPCR results, quality purified nucleic acids from different types of biological samples are required. Therefore, extraction techniques that allow to automate the process (e.g., those based on magnetic particles) are a good solution to quickly manage eluates for qPCR detection. Currently, due to the growth of these infections, different extraction techniques are emerging to automate the simultaneous processing of more and more samples.
Aim
This study aimed to determine the analytical performance and the clinical sensitivity and specificity of the VIASURE molecular diagnosis workflow (Automated extraction + PCR setup platform combined with qPCR test kits) for the detection of bacteria and AR in blood cultures. In addition, the workflow was summited to an external quality assessment (EQA) to confirm its specificity and sensitivity to detect resistance genes and different pathogens in respiratory samples.
Materials and methods
The assays were performed with VIASURE products: blood pathogens extraction kit (for blood samples and derivates), DNA/RNA pathogen extraction kit (for respiratory samples), V-Flex platform, V-Lab96 Cycler and 6 VIASURE qPCR detection kits. The extraction technology is based on the isolation of nucleic acids by binding them to superparamagnetic nanoparticles, so the workflow was compared with a similar extraction platform and kit of reference; MagDEA-Dx-SV.
The analytical sensitivity (limit of detection, LOD), linearity and precision were determined for *Klebsiella pneumoniae* by spiking negative blood cultures with a quantified reference strain (*ATCC-BAA-2146*). For the clinical evaluation, 68 blood culture samples from the Hospital Royo Villanova (Zaragoza) were analysed for 6 bacteria and 14 AR genes (n=816). For the EQA samples evaluation (IDPN-A-2023), 5 respiratory transport mediums from CAP (College of American Pathologists) were analysed for 17 viruses, 25 bacteria, and 9 AR genes (n=255).
Results
The LOD and linearity efficiency values for *K. pneumoniae* were 0.005 CFU/µL and 92.01% (R^2=0.96), respectively. Appropriate reproducibility and repeatability results were obtained (s<2 and CV%<10%). Clinical sensitivity and specificity were >95% for the 68 samples tested. Results were first compared with initial routine diagnosis and incongruent samples were resolved with results from the comparator kit, obtaining 35 positive samples for sepsis bacteria and 28 for AR genes. The diagnosis of the samples of the EQA programs agrees 100% with the results of the organizing college and was as follows: 1 virus, 5 bacteria and 2 AR genes.
Conclusion
The VIASURE complete workflow has demonstrated to be a fast, sensitive, and specific method in sepsis diagnosis and AR genes detection, shortening the turnaround time from several days to less than 3 hours. Further studies will evaluate the performance of the VIASURE molecular workflow with direct samples to paired culture samples, to reduce time in as it would avoid 1-5 days of blood culture incubation, speeding up the full diagnostic process.

YP-38

Revalorization of garlic (*Allium sativum* L.) by-products by pressurized liquid extraction

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Keywords: *Garlic by-products, Pressurized liquid extraction, Bioactive compounds, Revalorization*

Garlic (*Allium sativum* L.), widely consumed and appreciated for its organoleptic and bioactive properties, generates large volumes of waste, since it is usually marketed as the bulb, discarding the root, stem and leaves. A strategy to reuse these garlic residues would be to produce high added-value ingredients by extracting bioactive compounds such as organosulfur compounds (OSCs), bioactive carbohydrates (CHss), amino acids (aa), etc. Pressurized liquid extraction (PLE) is an efficient technique that has been widely applied for extracting bioactives from vegetal sources, as it usually provides a reduction in extraction time and solvent consumption as compared to conventional extraction techniques [Trac–Trends Anal. Chem.114 (2019) 314–325]. However, to the best of our knowledge, has been scarcely applied to extraction of bioactives from garlic bulb [Molecules 28 (2023) 369], and no studies regarding the simultaneous extraction of bioactive OSCs, CHs and aa from garlic waste for its revalorization have been reported. Thus, in this work, after selecting the optimal sample amount (100 mg) and extranctant (water), a response surface methodology based on a 3-level factorial design was used to evaluate the influence of extraction temperature (T) and time (t) (in the ranges 70-120°C and 5-30 min, respectively) on maximization of garlic bioactive extraction. To this aim, the different PLE extracts obtained under different T and t conditions were analyzed by liquid chromatography coupled to mass spectrometry (LC-MS) using different columns: a reverse-phase C_{18} for OSC and aa determination and a HILIC column for CHs analysis.
The maximum extraction of organosulfur compounds (1.28 $mg \cdot g^{-1}$ dry sample), prebiotic carbohydrates (24.12 $mg \cdot g^{-1}$ dry sample), and amino acids (7.58 $mg \cdot g^{-1}$ dry sample) was obtained under the following operation conditions: 18 min and 89 °C. These results demonstrated the feasibility of using PLE for obtaining extracts enriched in bioactive compounds from the waste generated in the manufacturing of garlic-based by using a green and efficient approach.

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YP-39

Hypercrosslinked β-cyclodextrins polymer as sustainable sorbent for the extraction of persistent organic pollutants from environmental water

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Keywords: *β-cyclodextrins, Nanosponges, Dispersive solid-phase extraction, Organic pollutants*

In recent years, the use of sustainable materials in sample preparation, in particular as extraction sorbents, has highly increased in order to compile with green analytical chemistry (GAC) principles [Trac–Trends Anal. Chem. 50 (2013) 78–84]. Besides, new trends are also focused on the use of safe and non-toxic sorbents, in combination with microextraction techniques, which will also highly reduce solvent and reagents consumption.
In this work, a sustainable, harmless, biodegradable, and inexpensive sorbent based on β-cyclodextrins (β-CDs) has been synthesized without the addition of any organic solvent, using citric acid as the crosslinker and sodium dihydrogen phosphate as the catalyst. The hyper-crosslinked obtained polymer, called as "nanosponge" (NS), was characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), infrared spectroscopy, BET surface analysis, and scanning electron microscopy (SEM). The obtained nanostructured β-CD-NSs (which show a high hydrophobicity) were used as dispersive solid-phase extraction (dSPE) sorbents of several persistent organic pollutants (i.e. polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorine pesticides, organophosphorus esters, UV filters and antibacterial agents) from environmental waters samples (i.e. sea and waste water). After optimization of the extraction conditions, by using only 30 mg of NS, recovery values ranged between 58 and 121% with relative standard deviation values below 20% for most of the analytes.

YP-40

Vertical introducing bio-compatible solid-phase microextraction pin to mass spectrometry using probe electrospray ionization interface for high sensitivity and low matrix effect analysis

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Keywords: *Solid-phase microextraction pin, Probe ionization, Mass spectrometry, Bio-compatible coating, Matrix effect*

Probe ionization mass spectrometry (PESI) using an ultrafine needle to sample extremely small volume of sample on its surface and subsequently applying high voltage to initiate ESI, forming nano droplets with reduced matrix effect. The sensitivity of PESI-MS can be an issue because the amount of ions generated is limited. Herein, SPME pin-PESI device with large diameter and bio-compatible SPME coating on the surface was proposed for increasing the sensitivity of PESI-MS by increasing the picked-up volume and enrichment effect of SPME, while minimizing matrix effect because selectivity of the biocompatible coating. The new design was applied for the analysis of 8 drugs of abuse in urine samples with the good linearity ($R^2 \geq 0.9997$), high sensitivity with limits of detection (LODs) between 0.003 to 0.03 ng/mL and good reproducibility with RSD% ≤ 6%. The vertical design of the SPME-MS direct coupling interface also opens a new insight of the potential fully automation of the entire system using autosampler. A stainless-steel pin device with diameter of 1.5 mm and cone length of 5 mm was coated with a thin layer of biocompatible SPME coating on the cone part. The coating consisting of hydrophilic-lipophilic balanced (HLB) particles embedded in polyacrylonitrile (PAN) binder. After extraction for 30 min by direct immersion in the sample with vortex and brief washing with water for 5 s, the SPME-pin device was directly insert into the Shimadzu DpiMS source for automated desorption and ionization by pick-and-spray strategy. The SPME pin-PESI device was compared with the previous SPME probe-PESI and PESI device regarding the sensitivity and linearity by analysis of several drugs in urine samples.

The pin device is compatible with the Shimadzu DPiMS source and does not need any modification of the MS instrumentation. Without coating material, the new pin design showed much higher sensitivity than the original PESI device when analysis the same concentration of the target drugs in solvents, as the pin device which has larger diameter can pick up more sample after dipping. After coating, a thin bio-compatible coating material (HLB/PAN) can be immobilized on the pin device. The SPME pin can be directly used in biological samples, as the PAN acts as both a binder and a matrix-compatible barrier, thus enabling the enrichment of small molecules while eliminating interferences associated with presence of interfering macromolecules. For the extraction of 8 drugs in the same PBS solutions, the extracted amount of the new SPME pin device was 22-82 times higher when compared with the previous SPME probe-PESI device because of the larger volume of coating material. Both of the above two factors, including more pick-up volume and higher extraction efficiency, made the SPME pin-PESI-MS show significant improvement of sensitivity when compared with the PESI-MS and the coated original SPME-PESI device reported previously. Finally, the SPME pin-PESI-MS method was used for the quantitative analysis of 8 drugs in urine samples, this new method showed 166-1666 times lower LODs when compared with the PESI-MS method, which demonstrated its ultra-high sensitivity. The SPME pin-PESI-MS method also showed good linearities with $R^2 > 0.9997$. In addition, the vertical arrangement of the SPME pin-PESI-MS system facilitates future fully automated and high-throughput analysis by incorporating with CTC autosampler system.

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YP-41

Mixed-mode cationic exchange sorptive tapes combined with mass spectrometry for determinating drugs of abuse in saliva samples

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Keywords: *Polymeric particles, Thin-film microextraction, Mass spectrometry, Drugs of abuse*

The work describes the use of mixed-mode cationic exchange (MCX) tapes as sorptive phases in bioanalysis. The tapes are synthesized using aluminum foil as substrate, which is subsequently covered with double-sided adhesive tape where the MCX particles adhere. This approach allows using this sorptive phase in thin-film microextraction (TFME), requiring a low amount of MCX particles and simplifying the extraction procedure, as the particles can be quickly recovered for the final instrumental analysis. The tape is incubated in a vial with the sample under continuous stirring to isolate the analytes. The agitation is performed in an orbital shaker, thus allowing the simultaneous extraction of several samples providing a high sample throughput. The results have demonstrated that MCX particles are mainly responsible for extracting the analytes (basic drugs), while the contribution of the aluminum-adhesive substrate is negligible. Moreover, three different eluents have been studied (methanol, methanol/ammonia (99/1 v/v), methanol/formic acid (99/1 v/v)), to break the interactions between the sorptive tapes and the analytes. Different variables related to the extraction procedure have been evaluated (agitation rate, ionic strength, extraction time, and dilution factor), and some have been studied using a multivariate approach.
Two different analysis workflows have been evaluated. In the simplest one, the tapes follow conventional solvent elution, and the resulting eluates are analyzed by direct infusion mass spectrometry. In the second approach, the direct analysis of the tape by substrate-spray ambient mass spectrometry has been studied. The preliminary results are promising, and the versatility of the approach will permit its adaptation to different analytical problems.

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YP-42

Metal-organic frameworks as sorbents for the antidepressant vortioxetine via miniaturized dispersive solid-phase extraction and high-performance liquid chromatography with diode array detection

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Keywords: *Antidepressants, Biological analysis, Metal-organic frameworks, Adsorption kinetics, High-performance liquid chromatography*

Antidepressants are chemical compounds used in medicine for the treatment of anxiety and depression, among other health disorders. Selective serotonin reuptake inhibitors (SSRI) and serotonin and norepinephrine reuptake inhibitor (SNRI) are the antidepressants most extensively used. These pharmaceuticals are prescribed together to ensure proper efficiency in the treatment and to avoid the development of resistance.
Despite their benefits, antidepressants have some drawbacks, mostly coming from their misuse and their relatively easy access. For these reasons, it is useful to develop a simple methodology to monitor the levels of antidepressants in non-invasive human samples, like urine or saliva. In these types of complex samples, the extraction and preconcentration of these analytes is essential to ensure a sensitive determination.
Metal-organic frameworks (MOFs) are materials formed by the coordination of metallic centres with organic ligands, generating a crystalline material with permanent porosity and impressive surface areas. Despite the excellent properties of these materials as sorbents, the selection of a particular MOF for a specific application is a very difficult task. For this reason, we propose a protocol to evaluate the efficiency of a battery of MOFs in a miniaturized dispersive solid-phase extraction (μ-dSPE) towards the extraction/desorption of a model analyte belonging to the antidepressant family, specifically vortioxetine. Besides, MOFs of the UiO and MIL families were evaluated, being synthesized through solvothermal methods, and characterized through X-ray diffraction and Fourier transform infrared spectroscopy. These MOFs are based on Zr(IV) and Fe(III) metal ions and different organic ligands, with pore diameters in the range 0.75 to 3.4 nm, being the UiO-66(Zr) the MOF with the smallest surface area and MIL-101(Fe) the one with the highest. Their efficiency in the adsorption of vortioxetine was evaluated through adsorption kinetic experiments. Furthermore, the MOF stability in urine was studied to propose these materials for biomonitoring studies. The analytical method for the antidepressant vortioxetine proposed is based on μ-dSPE, followed by high-performance liquid chromatography with diode array detection.

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YP-43

Determination of the modification of *Lactuca sativa* L. leaves' metabolic profile due to the presence of bisphenol A in the hydroponic media by UAE-GC-MS

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Keywords: *Metabolomics, Bisphenol A, Lettuce, Gas chromatography-mass spectrometry, Hydroponics*

Bisphenol A (BPA) is an organic compound used for the fabrication of polycarbonate plastics and epoxy resins [Sci. Total Environ. 655 (2019) 607–613]. Because of its high global annual production volume, which was expected to rise to 10.8 million tons by 2022 [ACS Omega 3 (2018) 6523–6532], and its transference to the environment due to contact between superficial or residual waters and products that contain it, BPA has become a ubiquitous contaminant which has been determined in different environmental and biological matrixes such as water, soils, sediments, dust, plants and human tissues, blood, serum and maternal milk [Chemosphere 268 (2021) 129273; Environ. Sci. Technol. 50 (2016) 5438–5453]. BPA's toxicity to plants has been reported in the literature [J. Hazard. Mater. 384 (2020) 121488], however, there is a knowledge gap in the study of the compound's direct effect to their metabolism.

Metabolomics is branch of omics sciences which focuses on the analysis of low molecular compounds (< 1500 Da) which take part in biochemical reactions required for organisms' general functioning and is a great tool to evaluate the metabolic alterations produced to a biological system by the presence of organic contaminants [Trac–Trends Anal. Chem. 24 (2005) 285–294]. Gas chromatography coupled to mass spectrometry (GC-MS) is one of the various instrumental techniques used in metabolomics because of its high-resolution separations and its ionization and fragmentation reproducibility, which leads to the aid of mass spectral libraries for metabolites' identification [J. Hazard. Mater. 373 (2019) 527–535]. Despite its difficulty in analyzing non-volatile compounds, GC-MS has proved to be able to determine a wide enough array of metabolites to detect the metabolic modification due to a determined stress in an organism [Anal. Chim. Acta 1210 (2022) 339043].

For the evaluation of *Lactuca sativa* L. leaves' metabolic profile, they were cultivated in the laboratory from the seed by the hydroponic floating root method, using a LED lamp to replace sun irradiation in cycles of 14 hours of light and 10 hours of darkness. 26 days after sowing, 18 lettuces were chosen and separated in three different groups: control and fortified with BPA in the hydroponic media at an environmental relevant concentration (5 ng/mL) and a higher concentration than the previous one (5 µg/mL). No physical differences were observed between lettuces from each group during their growth. 54 days after sowing, six leaves of each lettuce were harvested, immediately immersed in liquid nitrogen, freeze dried for 48 hours, homogenized in an agate mortar and stored in a desiccator until their analysis.

To ensure that a wide metabolic profile would be determined, four different analytical methods were developed for the determination of lettuces leaves' metabolic profile, varying mainly between them the implemented extraction solvent and derivatization procedure. Ultrasound-assisted extraction (UAE) was applied for sample preparation. Method development by UAE-GC-MS was focused on miniaturization, as only 5 mg of sample, 5 mL of solvent and 150 µL of other reagents were required for the analysis of each sample. Developed method's repeatability was evaluated by analyzing control lettuce leaves by sextuplicate obtaining relative standard deviations (RSD) lower than 30% for almost all the components detected in the obtained chromatograms, which is considered as acceptable by some metabolomics protocols by GC-MS reported in the literature [Anal. Chim. Acta 1210 (2022) 339043; Curr. Protoc. Mol. Biol. 114 (2016) 30.4.1–30.4.32].

After raw data processing, principal component analysis (PCA) and partial least squares – discriminant analysis (PLS-DA) were applied observing group separation in the score plots, which demonstrated that there is a metabolic change in lettuces' leaves due to the presence of BPA in the hydroponic media. Identification of the most important metabolites for group segregation was done by a four-level confidence scale based in literature reports [J. Anal. Appl. Pyrolysis 156 (2021) 105112; Bioanalysis 1 (2009) 1579–1596]. The possible affected metabolic pathways were predicted. These results show that organic contaminants, which are present in the environment at a wide range of concentrations, can alter plants' metabolism even when no physical changes or diseases are apparent in the organism.

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YP-44

Levels of 16 urinary phthalate metabolites in adult population of Valencia Region (Spain)

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Keywords: *Biomonitoring, Urine, Phthalates, Liquid chromatography, Mass spectrometry*

Phthalates are used as plasticizers in many applications such as food contact materials, clothing or flooring. They can be released into the environment by leaching and migration. Population is exposed to them through ingestion, inhalation and dermal contact. After entering the human body, they undergo phase I and phase II metabolism and are excreted in urine after a few hours. Since several studies have suggested that they can have toxic effects on reproduction and are possible endocrine disruptors in humans, it is necessary to assess human exposure to these plasticizers. In order to study global exposure to phthalates, quantification of phthalate metabolites in urine is the best choice to assess recent exposure.
In the present study, a method based on liquid chromatography coupled to triple quadrupole tandem mass spectrometry was applied to determine sixteen urinary phthalate metabolites in samples of 537 adults from Valencia region (Spain). Samples were collected during 2021.
Ten out of sixteen metabolites showed detection frequencies >65%, whereas the rest of metabolites had low detection frequencies (<40%) and three of them were not detected in any sample. The concentrations ranged from <0.5 (LOQ) to 61.50 ng/mL and monoethyl phthalate showed the highest concentrations, with a geometric mean of 39.81 ng/mL.
In general, phthalate metabolite concentrations quantified in the present study were lower than concentrations described in previous studies developed in Valencia Region which involved lactating mothers and children populations. Furthermore, levels of most of the phthalate metabolites were lower than in previous international studies involving general population such as in USA or Canada.

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YP-45

Analytical assessment of forage quality: A case study on native flora from Fuerteventura (Canary Islands, Spain)

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Keywords: *Forage quality, Nutritional analysis, Ruminant nutrition, Digestibility, Fatty acid composition*

The Canarian archipelago, especially in its most arid territories such as the island of Fuerteventura, faces a deficit in the production of feed for livestock, importing from the mainland practically all the forage consumed by a large goat herd [ISTAC, 2022]. In the last decades, there has been a growing interest in identifying new forage species from native flora in arid and semiarid regions [Agric. Water Manag. 199 (2018) 11–21]. These species must not only adapt to challenging environments (e.g., water stress, salinity, low nutrient content), but also meet the nutritional needs of livestock over extended periods and provide specific nutrients that can enhance livestock health and add value to derived products like meat and dairy [Foods 11 (2022) 646]. Therefore, the assessment of forage quality is essential for animal nutrition as it directly impacts their dietary requirements [Front. Plant Sci. 9 (2018) 535]. This study focuses on several analytical methodologies to measure key parameters such as protein and fiber contents, and lipid profiles, which are crucial indicators of forage quality. The research focused on the native flora from Fuerteventura Island including four legumes (*Lotus lancerottensis, Bituminaria bituminosa, Coronilla viminalis* and *Retama rhodorhizoides*), three grasses (*Cenchrus ciliaris, Phalaris coerulescens* and *Tricholaena teneriffae*) and five other herbaceous and shrub species from different families (*Lavatera acerifolia, Periploca laevigata, Campylanthus salsoloides, Echium decaisnei* and *Crambe sventenii*). All species were cultivated in nursery and sampling of vegetal tissues (leaves) was carried out in November 2021 when plants were 10-18 months old. Once in the laboratory, each sample of plant material was divided into two subsamples. One of the subsamples was dried at 60 ºC for 72 h and ground and sieved (< 1 mm) for fiber and protein analysis, and the other subsample was stored at -80 ºC until the moment of carrying out the lipid analysis. Fiber content was assessed using the detergent system, which partitions feeds into fractions to predict their nutritional value. The nutritional potential of the forages was evaluated based on ash content, neutral detergent fiber (NDF), acid detergent fiber (ADF), crude protein (CP), and enzymatic organic matter digestibility (EOMD). Lipid extraction was performed using chloroform/methanol (2:1, v/v) and then the total lipid content (TL) was gravimetrically determined after evaporation of the organic solvent under a nitrogen atmosphere. Lipid classes were separated by one-dimensional double-development high-performance thin-layer chromatography (HPTLC) and quantified by calibrated densitometry by reference to external lipid standards. Fatty acids methyl esters were obtained through acid transmethylation of a lipid aliquot and determined by gas chromatography (GC). Results showed that the highest NDF and ADF values were observed for grasses. Conversely, as expected, legumes generally had higher CP and TL contents than the other families. All species had a high proportion of polyunsaturated fatty acids (PUFA), mainly α-linolenic acid (18:3 n-3, ALA) and linoleic acid (18:2 n-6, LA). In addition, the presence of beneficial molecules for animal health such as γ-linolenic acid (18:3 n-6, GLA) in *E. decaisnei* and the large levels of phytosterols (PTS) in *C. sventenni* must be highlighted. Most of the species studied had a similar or a slightly lower nutritional value compared to conventional forages such as alfalfa. Therefore, it is concluded that the evaluated native species pool has potential as an alternative feed for ruminants when forage shortages.

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YP-46

Employing the statistical experimental design for the optimization of low volume-SPME for analysis of volatile organic compounds in exhaled breath condensate by GC-MS

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Keywords: *Breath, Volatiles, Metabolomics, Volatilomics*

Over the last few years, the analysis of breath is gaining increasing interest. Exhaled breath contains more than 1000 volatile organic compounds (VOCs), which can inform about the metabolic state of the body and the development of any pathological states. However, the analysis of breath is challenging, especially in the sample collection state. The most commonly used method is the application of Tedlar gas sampling bags, which when inflated are problematic in terms of transportation and storage. An alternative for breath sampling is the collection of exhaled breath condensate (EBC). EBC is the exhalate from breath, that has been condensed, typically via cooling using a collection device to a small volume of liquid. EBC reflects the composition of the airway lining fluid and alveoli and also mixes with salivary and gastric droplets. Notably, since EBC is collected in liquid form, it is much easier to transport and requires less place to store. However, the collecting of EBC is exhaustive for individuals and breathing can be conducted only for a few minutes. Consequently, the volume of EBC is relatively low and it requires a sensitive method capable of extraction even from a small volume.

The aim of this study was to optimise solid-phase microextraction (SPME) for analysis of VOCs in EBC using gas chromatography-mass spectrometry (GC-MS). The mixture of 14 authentic standards of compounds previously detected in breath samples, differing with the chemical properties was prepared for optimization. The optimized parameters included type of fibre, mode of extraction (headspace vs. direct immersion), time of equilibration, and time and temperature of extraction. In the first step, the screening experiment comparing different fibres (CAR/PDMS, DVB/CAR/PDMS and DVB/PDMS) and modes were compared. The extraction was conducted in 2 mL vials from 200 µL sample volume. For direct immersion, 200 µL inserts were applied. The fibres were immobilized above the vials using a home-made device and the samples were equilibrated for 10 min at 40 °C with 250 rpm shaking, then extracted for 10 min at the same temperature, and finally desorbed for 10 min in the GC injector port.

The most optimal fibre was selected for further optimization using the design of experiment (DoE) approach. The analytical performance of the optimized method was evaluated in terms of precision, accuracy and linearity. Finally, the optimised method has been successfully applied for the quantitative analysis of real samples collected from 3 subjects using GC-MS as well as volatilomic profiling using GC×GC-TOFMS.

The optimized method can be applied for the routine analysis of EBC to early detection of diseases and tracking of metabolic changes caused by lifestyle changes.

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YP-47

Automated microfluidic open interface for direct coupling of solid-phase microextraction to mass spectrometry to facilitate rapid and high-throughput analysis

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Keywords: *Microfluidic open interface, Mass spectrometry, Solid-phase microextraction, Automation*

Microfluidic open interface (MOI) is a sample injection interface which operates under the concept of flow-isolated sample injection chamber with the solvent delivery system. The MOI can be directly connected with ESI or APCI sources for MS sampling (MOI-ESI/APCI-MS). MOI-MS is an ideal interface for direct coupling solid-phase microextraction (SPME) to MS for rapid analysis (less than 50 s per sample). The interface provides a small desorption chamber and constant liquid flow to MS with stable ionization. Herein, the MOI-MS interface was redesigned using a simple three-port tee with reduced dead volume, and the system automation was realized by using a software-controlled solvent delivery system, allowing for reproducible sample injection.
A three-port tee was used to make MOI-MS interface instead of the complex co-axial tubes in the previous design, offering lower overall dead volume. For the automation, a photo interrupter was applied for recognizing the flow of liquid in the PTFE tubing by monitoring the adsorption value inside the tubing with infrared ray (IR) and providing a signal to the data acquisition device connected to the computer. Homemade software was used to control the delivery of solvents into the MOI-MS interface via a programmable syringe pump after getting the signal from the data acquisition device. After coupling with automated 96 concept SPME system, a high-throughput SPME-MOI-MS method was developed for the rapid analysis of 16 drugs of abuse in human saliva samples.
The new design with standard chromatography-used three-port tee and tubes makes the interface can be easily manufactured and connected with different ESI interfaces tested on Shimadzu, SCIEX and Thermo MS instruments. The automation of the MOI-MS interface can not only save labor time, but also significantly improve the reproducibility of the SPME-MOI-MS method with the RSD% ≤ 7% (n=9). The MOI-MS interface provides a continuous and stable electrospray fluid flow to the MS without generating any bubble, a feature that we exploit to introduce the concept of multi-segment injection for the determination of multiple samples in a single MS run. High-throughput and automated SPME system (sample preparation of 96 samples simultaneously) was coupled directly to MS via MOI for the fast analysis of 16 drugs of abuse in human saliva samples. With the above strategy, the average total analysis time for each sample, including sample preparation and MOI-MS analysis is 75 s. The developed method provides good analytical performance, with LODs ranging between 0.05-5 ng/mL, good linearity (R^2 ≥ 0.9957), accuracy between 81 and 120%, and good precision (RSD% < 13%) for the analysis of 16 drugs of abuse in human saliva samples. Additionally, a proof-of-concept experiment was designed for demonstrating the capability of the SPME-MOI-MS method for real-time detection of threshold substances from WADA prohibited list, to show the potential of the method for rapid on-site anti-doping test.

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YP-48

Comparison of different stationary phases of solid-phase extraction (SPE) for efficient isolation of 8-isoprostane and 8-hydroxyguanosine from exhaled breath condensate and urine

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Keywords: *Breath, Oxidative stress, Solid-phase extraction, 8-isoprostane, 8-hydroxyguanosine*

Oxidative stress is a common mediator for the development of many diseases, including cardiovascular diseases (CVD). Reactive oxygen species generated during oxidative stress lead to cell dysfunctions, necrosis or apoptosis, as well as post-translational modifications altering signalling pathways. Individuals suffering from obesity have increased oxidative stress and consequently have a higher risk of CVD. Therefore, the measurement of oxidative stress became a promising tool reflecting the disease progress. There are many methods and markers used for the estimation of oxidative stress. They can be divided into endogenous antioxidants, such as catalase and superoxide dismutase; markers of protein peroxidation, such as m/o-tyrosine, protein carbonyls, biomarkers of lipid peroxidation, such as malonaldehyde and F_2-isoprostanes and finally markers of nucleic acid peroxidation, including 8-hydroxyguanosine (8-OHdG). Two relatively new markers, which are gaining big interest are 8-OHdG and 8-isoprostane, which belong to sensitive markers of oxidative stress, which level can be measured noninvasively in urine. Moreover, recent studies showed that these two biomarkers can be measured also in exhaled breath condensate (EBC).

Therefore, the aim of this study was to optimize the solid-phase extraction (SPE) method for the isolation of 8-OHdG and 8-isoprostane from urine and EBC. Five types of reversed-phase polymeric sorbents, including C8, C18, C18e, LEOX and HLB (BEKOlut, Bruchmuhlbach-Miesau, Germany) were compared in this study in three types of matrices: urine, EBC and aqueous standard mixture. The mass of sorbent (200 mg) and sample volume (3 mL) were not optimized and remained at the same level for the whole experiment. In the next step, different elution solvents have been compared (ethyl acetate, methanol, ethanol, acetonitrile). Samples of EBC and urine have been obtained from three healthy subjects and pooled for optimization purposes. Extraction efficiency was determined by HPLC with diode array detection (DAD).

Using the selected sorbent and elution solvent, it was possible to quantify 8-isoprostane and 8-OHdG in the analysed body fluid.

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YP-49

Harnessing the potential of natural compounds through DES-based DLLME to make greener fragrance analysis: A case study with high water content samples

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Keywords: *Natural hydrophobic eutectic solvent, Dispersive liquid-liquid microextraction, Gas chromatography, Fragrances*

Gas chromatographic analysis of possible cross-contaminations in perfumes is routinely performed in fragrance quality control laboratories. Conventional analytical methods require either the use of large amounts of organic solvents, or the direct injection of samples, which can lead to interferences and/or require frequent maintenance of the chromatographic system, especially when high water content fragrances are analysed.
In this work, a more environmentally friendly approach for the extraction and enrichment of volatile compounds from aqueous perfumes is proposed. The method is based on dispersive liquid-liquid microextraction (DLLME) using a natural-based deep eutectic solvent (DES) as extraction solvent. This new class of natural solvents is characterized by simplicity in synthesis, low cost, environmental friendliness, and (in some cases) natural origin, so it can replace traditional organic solvents. Here, hydrophobic deep eutectic solvents (HDES) consisting of volatile terpenoids and phenols isolated from essential oils and/or other natural products are studied. These natural HDES can be used for the extraction of aqueous samples and, because of their volatility, can be analyzed directly by GC (and GC-MS). The application of HDES in dispersive liquid-liquid microextraction (DLLME) for the extraction of possible cross-contaminants from hydroalcoholic commercial fragrances makes it possible to obtain enrichment factors and analytical figures of merits suitable for their determination, as required in quality control laboratories.

YP-50

Metal-organic frameworks and biopolymers for the extraction of anthraquinones and chromones in aloe vera gel via miniaturized dispersive solid-phase extraction and high-performance liquid chromatography with diode array detection

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Keywords: *Aloe vera, Biopolymers, Miniaturized dispersive microextraction, Metal-organic frameworks, Phenolic compounds*

Aloe vera is a medicinal plant known for its wide variety of therapeutic properties, which make it of great interest in the cosmetic, food and agriculture industries. Among these properties, it is important to mention the anti-inflammatory, anti-cancer and antioxidant effects. Thus, aloe vera products can help to relieve constipation, reduce the inflammation, promote wound healing, protect against cellular damage caused by free radicals, and potentially prevent the growth and spread of cancer cells. These benefits are the result of the presence of a wide variety of naturally occurring compounds such as certain phenolic compounds known as anthraquinones and chromones. However, other compounds also present in the plant can cause negative effects. For example, anthraquinones such as aloins are regulated by the European Union Regulation (CE) nº 2021/468 of March 18 because of their *in-vivo* genotoxic and laxative effects.

Most of the analytical methods for the monitorization of these and other bioactive compounds are based on solid-liquid extraction from the aloe vera leaves in combination with liquid chromatography. These sample pretreatment strategies are tedious and time consuming, and often require of the use of copious amounts of toxic organic solvents. Sorbent-based (micro)extraction techniques can be implemented to overcome all these issues.

Metal-organic frameworks (MOFs) are crystalline solids consisting of metal ions or metal clusters and organic ligands linked by strong coordination bonds. Their main characteristics depend on the selected organic ligands and their connectivity in the structure, together with their porosity, particle size, and nature of the metal cluster, among other factors. Biopolymers are polymers obtained from natural sources and constitute a renewable and biodegradable resource of materials. This group includes polysaccharides, proteins and lipids derived from animals and plants. Both materials are of special interest in analytical sample preparation because they can be employed as sorbents for the extraction and preconcentration of different organic compounds.

The aim of this study is to test de suitability of non-conventional sorbents for the extraction of anthraquinones and chromones in aloe vera gel. The analytical method proposed in this study is based on miniaturized dispersive solid-phase extraction (μ-dSPE), followed by high-performance liquid chromatography with diode array detection (HPLC-DAD). Different types of MOFs and biopolymers will be studied as possible extraction sorbents.

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YP-51

Solid-phase immunoextraction followed by liquid chromatography-tandem mass spectrometry for the selective determination of thyroxine in human serum

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Keywords: *Human serum, Immunosorbent, Liquid chromatography-tandem mass spectrometry, Solid-phase extraction, Thyroxine*

Thyroxine (T4) is a tyrosine-based hormone produced by the thyroid gland. The main function of this thyroid hormone is to regulate biological processes in humans such as growth and development, basal metabolism, or reproduction. The normal serum concentration of total T4 ranges from 60 to 160 nM (*i.e.*, 47 to 124 ng·mL^{-1}). However, people that suffer from thyroid-related diseases present abnormal levels of T4, causing hypo- or hyperthyroidism. Several health conditions can induce these disorders, such as autoimmune diseases (*e.g.*, Hashimoto or Grave's diseases) or thyroiditis. Therefore, the determination of T4 is important to monitor its levels, which should be within the normal range, showing the proper functioning of the thyroid gland.
In this communication, an analytical method based on solid-phase extraction (SPE) followed by liquid chromatography-tandem mass spectrometry analysis (LC-MS/MS) has been developed for the selective determination of T4 in human serum. For this purpose, two immunosorbents specific to T4 were synthesized by grafting two different T4-specific monoclonal antibodies on cyanogen bromide (CNBr)-activated-Sepharose® 4B as solid support. The grafting yields obtained from the immobilization of each antibody on the CNBr-activated-Sepharose® 4B were over 90%, demonstrating that most of the antibodies were covalently bound to the solid support. The SPE procedure was optimized by studying the retention capacity and selectivity of the two immunosorbents in pure media spiked with T4. Under the optimized conditions, high elution efficiencies were achieved in the elution fraction for both specific immunosorbents (*i.e.*, 85%), whereas low ones were obtained in the control immunosorbent (*ca.* 2%), showing the selectivity of the specific immunosorbents. The immunosorbents were also characterized by studying extraction and synthesis repeatability (RSD < 8%), and capacity (104 ng of T4 per 35 mg of immunosorbent, *i.e.*, 3 μg·g^{-1}).
Finally, the methodology was applied to a pooled human serum sample in order to study its analytical utility and accuracy. Relative recovery (RR) values between 81 and 107% were obtained, showing no matrix effects during the global methodology. Furthermore, the need to perform the immunoextraction was evidenced by comparing the LC-MS scan chromatograms and RR values with and without applying the immunoextraction procedure on a serum sample submitted to protein precipitation. This work exploits, for the first time, the use of an immunosorbent on the selective determination of T4 in human serum samples.

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YP-52

High-throughput determination of oxidative stress biomarkers in saliva by solvent-assisted dispersive solid-phase extraction for clinical analysis

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Keywords: *Bioanalysis, Dispersive-based microextraction, Hydrophilic-lipophilic balance polymer, Oxidative stress biomarkers, Saliva*

Oxidative stress is produced as a result of a disturbance in the oxidant-antioxidant balance in the organism, when reactive oxygen species are not completely inactivated by cellular antioxidant defenses. The determination of oxidative stress products in biological fluids, considered as potential biomarkers of diseases, have gained prominence in the field of medicine as tools for early diagnosis and disease control. 8-hydroxy-2'-deoxyguanosine (8-oxodG) and 8-hydroxy-2'-deoxyadenosine (8-oxodA), formed by oxidative DNA damage, are some of these numerous interesting oxidative stress biomarkers since they are commonly associated with diabetes and different types of cancer.

In this communication, a reliable analytical method for the simultaneous determination of these two oxidative stress biomarkers in saliva samples is presented. The method is based on solvent-assisted dispersive solid-phase extraction (SA-DSPE) as a clean-up step, followed by liquid chromatography-tandem mass spectrometry (LC-MS/MS). For this purpose, a commercial polymer with a hydrophilic-hydrophobic balance has been used as extraction phase. This balance makes the material suitable for extracting compounds from polar matrices such as saliva. Those variables involved in the extraction were optimized by a Box-Behnken design, whereas those variables affecting the desorption were optimized by a Doehlert design, except the desorption solvent that was optimized by using a Simplex-Centroid design. The method was successfully validated, showing a good linearity at least up to 20 $ng \cdot mL^{-1}$, limits of detection and quantification at the low $ng \cdot mL^{-1}$ level, and good repeatability values (< 15%). Standard addition calibration was employed to correct the observed matrix effects. Finally, this new approach was successfully applied to saliva samples from nine volunteers, three of them with type II diabetes, obtaining notable differences in the concentration values between both groups. The proposed methodology overcomes some of the drawbacks of the only previous work with the same purpose, such as the time-consuming procedure and the consumption of large volumes of organic solvents. To increase the sample throughput and reduce the analysis time, a thermostatic stirrer that allows the extraction of up to 24 samples simultaneously was used.

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YP-53

Octanol-supported wooden tips: Porous sorptive phases and organic solvent holders in microextraction

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Keywords: *Bioanalysis, Mass spectrometry, Non-steroidal anti-inflammatory drugs, Octanol-supported wooden tips*

Using natural materials (paper, cotton, cork, wood) and biopolymers (chitosan, alginate, agarose) as sorptive phases has been widely reported. The lignocellulosic nature of wooden tips combined with their inherent porosity allow the isolation of organic compounds from different matrices and the modification of their surface to boost the sorbent-analyte interactions. In this work, we describe the use of wooden tips in a dual role: they can act as a sorbent to isolate the target compounds and as a solid substrate to host an organic solvent (1-octanol) in their pores, boosting the extraction efficiency. Consequently, a mixed-mode extraction based on solid-phase and liquid-phase microextraction is presented. Regarding the well-known properties of 1-octanol in liquid-liquid extraction and partition coefficients, non-polar compounds such as non-steroidal anti-inflammatory drugs (logP 2.8-4.5) were chosen as model compounds.
The synergistic effect of octanol-supported wooden tips compared to bare wooden tips was studied. Moreover, the different variables that affect the extraction of the analytes (pH, ionic strength, and extraction time) were studied by HPLC-UV. The optimized extraction parameters were pH 3, 1.5 mL of 1:4 diluted saliva, and 30 min of extraction time. Although eliminating the chromatographic separation would speed up the extraction procedure, the leaching of intrinsic compounds associated with the wooden matrix implied an ion suppression that limited this approach. Therefore, liquid chromatography was compulsory to separate the leaching compounds from the analytes.
Under the optimized extraction parameters, the proposed method was validated in HPLC-MS/MS in terms of limits of detection, limits of quantification (8-32 µg/L), linear range (LOQ-1600 µg/L), linearity with $R^2 > 0.9924$, precision values (expressed as relative standard deviation) lower than 21.3%, and accuracy values (expressed as relative recovery) between 80 and 114%.

Acknowledgements
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YP-54

Natural materials and hypodermic needles in ambient ionization mass spectrometry: Affordable and disposable ESI emitters in bioanalysis

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Keywords: *Ambient ionization mass spectrometry, Bioanalysis, Cotton, Hypodermic needles, Polydopamine*

Sample preparation is an essential tool in microextraction to reach the required sensitivity and selectivity levels. In this context, mass spectrometry (MS) is strongly recommended when analyzing complex samples. Although MS is usually associated to a prior chromatographic separation, this step limits the sample throughput. The chromatographic separation can be substituted to a sample preparation process to extract the analytes and/or clean-up the sample. In this sense, the synergistic combination of sample preparation with ambient ionization mass spectrometry (AIMS) results into allow to speed up the analysis of the samples maintaining the analytical performance of the method. AIMS is an ionization mode performed at atmospheric pressure that can be classified into two main groups: electrospray (ESI)-based and atmospheric-pressure chemical ionization (APCI). Substrate spray belongs to the ESI-based group and consists of a sharp material (e.g. hypodermic needles) where the analytes had been deposited or extracted, and a metallic clip. When a spray solvent and a high voltage are applied, the analytes are on-line eluted and ionized entering into the MS inlet.

In this communication, we present the use of hypodermic needles as sorbent holders and ESI emitters in the analysis of oral fluid samples using natural materials as sorbents. The use of biopolymers as sorptive phases have been widely reported during the last years, including (ligno)cellulosic materials (e.g. paper, cotton, cork, wood), clay materials, chitosan, and alginate. In addition, natural monomers are used as precursors to form biopolymers (e.g. polydopamine). Hypodermic needles (HNs) are worldwide available and affordable (< 0.1 €/unit), allowing their disposable use to preserve the security of the operator and to avoid cross-contamination. Their sharp end combined with their metallic conductivity make them a suitable ESI emitter. Moreover, they can be simultaneously used as extraction device where the sorbent is immobilized or packed.

On a first approach, the inner walls of HNs were coated with polydopamine (PDA) to isolate methadone, cocaine, and methamphetamine from saliva. The geometry of HNs restricts the sorption capacity because the amount of sorbent was limited when flowing the sample through the PDA-coated HNs. Moreover, the kinetics of the extraction of the analytes was hindered as the mass transference was carried out on a small surface. To improve the initial extraction device, a porous composite based on cotton fibers coated with nylon-6 was developed using methadone as target compound. In this case, the sorbent-analyte interactions were enhanced by increasing the amount of sorbent and using a porous sorptive phase. The variables affecting the ionization of the analytes by the proposed AIMS interphase and the variables affecting the extraction process were studied. Finally, the proposed analytical methods were satisfactorily validated using in-matrix calibration curves in terms of limits of detection, limits of quantification, linear range, linearity, accuracy, and precision.

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YP-55

Encapsulation efficiency determination methods for the analysis of autoantigenic peptides within phosphatidylserine-liposomes

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Keywords: *Autoimmune diseases, PS-liposomes, Encapsulation efficiency, Autoantigenic peptides, Liquid-chromatography*

Autoimmune diseases (AIDs) are characterized by a malfunction of the immune system, which produces defective T and B cells that attack the own healthy tissues and cells. The prevalence of these illnesses is increasing and persists in individuals of all ages [Nat. Rev. Nephrol. 10 (2023) 1-16; Medicine – Programa de Formación Médica Continuada Acreditado 13 (2021) 1893–1905]. The development of a treatment that selectively eliminates the immune system autoreaction without affecting its normal functioning is not an easy task. Therefore, currently available palliative treatments are based on immunosuppressive and non-disease-specific strategies [Nanomed.-Nanotechnol. Biol. Med. 48 (2023) 102635]. In this regard, a novel nanotechnology strategy with specific encapsulated antigens in phosphatidylserine-liposomes (PS-liposomes) is being developed to achieve immunotolerance. The PS-liposomes structure mimics apoptotic cells, resembling the ability of the apoptosis process to induce immune tolerance. When PS (phosphatidylserine) interacts with phagocytes, cell apoptosis occurs and tolerance to the encapsulated autoantigens is promoted. This strategy results in a potentially curative approach.

Encapsulation efficiency (EE) in liposomal therapeutic formulations is a crucial quality attribute since the treatment's effectiveness usually depends on the amount of encapsulated drug. Furthermore, the presence of free drugs may result in undesired toxic side effects. The determination of encapsulated drug concentration can be accomplished indirectly, by subtracting free from total drug concentration, or directly, by isolation of the liposomes and subsequent lysis [Int. J. Pharm. 602 (2021) 120571]. Both strategies require the separation of the free drug from the encapsulated liposomes. Several methods were described in the literature for this purpose, most of them focused on the quantification of a single compound. However, studies comparing the performance of each method for different peptides are scarce.

In this study, peptides with different lengths and physico-chemical properties encapsulated in PS-liposomes were used as models to evaluate several methods for both free and total antigen quantification. Each of the selected peptides may induce immune tolerance against a different autoimmune disease: type 1 diabetes (T1D), celiac disease (CD), myasthenia gravis (MG) and multiple sclerosis (MS). For free antigen determination, a comprehensive comparison of different centrifugal filters (Amicon, Microcon, Vivaspin) was performed. The effect of filter passivation with bovine serum albumin (BSA) or polyethylene glycol (PEG) was also studied. On the other hand, the ultracentrifugation approach was also evaluated, and different conditions were tested to maximize recoveries. Finally, different methods for liposome lysis and subsequent total antigen quantification were also compared. Identification and quantification of the autoantigenic peptides were performed by reversed-phase high-performance liquid-chromatography with ultraviolet detection (RP-HPLC-UV). Results obtained for direct and indirect approaches were compared for PS-liposome samples. The best conditions for encapsulation efficiency determination of each antigen were selected.

YP-56

Isolation of PS-liposomes from biological samples by size exclusion chromatography and subsequent characterization

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Keywords: *Autoimmune diseases, PS-Liposomes, Extracellular vesicles, Size exclusion chromatography, Pre-concentration*

Autoimmune diseases approximatively affect twenty percent of the human population [Angum et al., 2020]. They are characterized by being chronic, complex, of unknown origin and currently they only have palliative treatments based on anti-inflammatories and immunosuppressors. In patients with autoimmune diseases, there is a failure in the peripherical tolerance recognition that ends up attacking their own cells or tissues [Mahajan et al, 2020; Pujol-Autonell et al., 2015]. The engulfment of apoptotic cells, which present phosphatidylserine (PS) in the outer membrane, by professional phagocytes results in the tolerogenic presentation of autoantigens (peptides) that induce specific tolerance. A novel curative treatment, taking advantage of this physiological process of tolerance generation, is being developed by bio-mimicking apoptotic cells. This is plausible by using PS-liposomes that encapsulate the peptides involved in the autoimmunity generation. In this way, tolerance against the own cells or tissues that were considered hostile can be achieved. In addition, only changing the encapsulated peptide is possible to treat different autoimmune diseases such as type I diabetes, rheumatoid arthritis, multiple sclerosis, or myasthenia gravis. The commercialization of PS-liposomes to treat autoimmune diseases first requires successfully completing the studies in the regulatory preclinical phase, whose main objective is the characterization of the safety and initial efficacy profiles of the new drug. For this purpose, trials are designed to study in animals the potential toxic or adverse effects of the product and to provide an estimation of the safe dose ranges for use in humans. Within these studies, it is necessary to develop bioanalytical methods capable to detect and quantify PS-liposomes in different biological fluids. Proper characterization of PS-liposomes in serum or plasma samples requires first their effective isolation. This isolation process is not an easy task due to the presence of protein aggregates, cells, and other extracellular vesicles in biological samples, which present similar composition or size to synthesized liposomes. Different methods for extracellular vesicles (EVs) isolation, most of them focused on exosomes, are described in the literature [Boriachek et al., 2019; Antes et al., 2015]. However, studies describing methods for liposome isolation in biological samples are scarce.

In this study, an isolation method using size exclusion chromatography (SEC) is described for non-loaded and loaded PS-liposomes from plasma samples. Two different columns were evaluated, Sepharose 2B-CL in-house packed column and new and improved agarose resin pre-packed cartridges from Izon Science Limited (Lyon, France). Different concentrations of PS-liposomes (0.5, 1 and 2 mM) were tested in order to maximize recoveries. Once the critical parameters of SEC were established, the separation method was applied to liposomes in plasma samples. The eluted fractions were analysed by flow cytometry to select the ones that contain liposomes. Preconcentration of SEC fractions was then assessed by two different methods: centrifugal filters Vivaspin filtrate from Sartorius (Göttingen, Germany) and Nanotrap particles from Izon Science Limited (Lyon, France), obtaining pre-concentration factors of x10 and x20, respectively. Finally, a liquid-liquid extraction procedure was applied to separate the lipids and autoantigen peptide of PS-liposomes from the rest of plasma compounds. The organic phase (bottom), which contains the lipids was analysed by HPLC-ELSD, while the aqueous phase, containing the encapsulated peptide, was analysed by HPLC-UV. The described methodology allowed a successful PS-liposomes isolation from biological samples and subsequent characterization.

YP-57

Characteristics of mixed chitosan-bioglass coatings on plasma activated PEEK polymer

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Keywords: *Biocoatings, Polyether ether ketone polymer, Surface properties, Biocompatibility assessment*

Polyether ether ketone (PEEK) is biocompatible, chemically and physically stable and radiolucent polymer that exhibits a similar elastic modulus to normal human bone, making it an attractive orthopedic implant material. However, PEEK is biologically inert, preventing enough strong bonding with surrounding bone tissue when it is implanted in-vivo. Surface modification and composite preparation are two main strategies to improve the bioactivity of PEEK. In this study, we prepared and investigated plasma activated PEEK surfaces with embedded bioglass, chitosan and chitosan-bioglass mixed layers applying dip coating/from solution hybrid coating technique.
The obtained surfaces were investigated in terms of wettability and surface free energy changes. Moreover, FTIR (Fourier transformation infrared spectrometry) and SIMS (secondary ion mass spectrometry) has been applied to establish and control coatings composition. Simultaneously the structure of coatings has been visualised with aid of SEM (scanning electron microscopy). Finally, the obtained systems were incubated in SBF (simulated body fluid) to verify the modifications influence on the bioactivity/biocompatibility of PEEK surface. For the preparation of bioactive PEEK composites, the main challenge is to keep the excellent mechanical properties of PEEK when impregnating bioactive materials, thus all conducted modifications affected only its upper surface. The development of PEEK composites covered with nano/micro-sized bioactive materials/films may provide an effective way to obtain both mechanical and biological benefits.

YP-58

A non-invasive colorectal cancer diagnostic method based on a solid-phase microextraction technique for the determination of organic compounds from fecal samples

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Keywords: *Colorectal neoplasms, Colorectal cancer, Solid-phase microextraction, Graphene oxide, Diet*

Colorectal cancer (CRC) was the third most common cancer worldwide and the second leading cause of cancer-related death in 2018. The estimated incidence increased for females in Spain last year [REDECAN, 2022]. The risk of CRC is influenced by environmental and lifestyle factors, such as diet, among others.
Currently, the screening test used for the diagnosis of CRC in Spain is the immunochemical fecal occult blood test (FIT), which is performed biannually in the population over 50 years old. If the FIT result is positive, a colonoscopy is performed, which is the clinical reference test in our country. The limitations of the FIT are the number of false negatives and positives that it provides, since it has a sensitivity and specificity of 66–87% and 65–95%, respectively. This fact causes that many patients suffers an unnecessary colonoscopy. Therefore, due to the limitations and drawbacks of both techniques (i.e., FIT and colonoscopy), it is interesting and necessary to develop more sensitive and specific non-invasive diagnostic methodologies to reduce the number of false positives and negatives, and thus avoid a large number of invasive screening tests such as colonoscopy.
On the other hand, the literature has demonstrated the relationship between CRC and the different profile of volatile organic compounds (VOCs) of fecal samples from control volunteers and CRC patients due to the dysbiosis and inflammation scenarios [Medicine 99 (2020) e20937]. Therefore, one of the objectives of this study is to develop a miniaturized methodology based on solid-phase microextraction technique using magnetic graphene oxide (MGO) and surface-modified MGO as sorbents to determine VOCs contained in fecal samples of CRC patients. The analytical system employed for separation and detection of the VOCs is a thermal desorption-gas chromatograph-mass spectrometer.
The methodology previously detected three VOCs in fecal samples (e.g., 1H-indole, p-cresol and 3(4H)-dibenzofuranone,4a,9b-dihydro-8,9b-dimethyl-) with good values of sensitivity and specificity 78-83% and 75-82%, respectively [Aparatos y métodos para el diagnóstico de cáncer colorrectal. P202030487 (2020); Clin. Chim. Acta. 542 (2023) 17273]. However, new compounds have been determined as potential markers of the CRC disease.
Regarding the results obtained until now, from the 18 control samples detected previously as false positives by FIT, only 3 have given false positives with our developed methodology. This fact could be related with the diet due to some differences in the intake of certain groups of food: such as an increased intake of red meat per week, high-fat content food, pastries, alcoholic beverages and soft drinks with sugar and pre-cooked foods.
In conclusion, colonoscopy remains the gold standard technique in clinical practice for the diagnosis of CRC. For this reason, the aim is to improve the knowledge about the different molecules present in feces that can be used as markers of CRC, and, therefore to develop a new non-invasive prevention and diagnosis methodology with better parameters of specificity and sensitivity than FIT; and thereby improve the prevention, management and treatment of the disease.

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YP-59

LC/MS determinations of kynurenine pathway metabolites in saliva

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Keywords: *Saliva analyses, Salivette technique, Liquid chromatography, Mass spectrometry, Kynurenine pathway*

Saliva is a fluid composed of water (99%) and several minor components including electrolytes, proteins (0.3%) and fatty acids [Anal. Bioanal. Chem. 414 (2022) 6899–6909]. Saliva is increasingly becoming the primary target for metabolic research and is gaining popularity as a potential tool for the diagnosis and monitoring of specific biological markers due to the fact that the concentration of metabolites shows strong correlations with plasma levels [J. Chromatogr. A. 1248 (2012) 178–181]. Tryptophan, kynurenine, and neopterin are specific biological markers that reflect the activation of immune system in different biological matrices such as serum, saliva, or urine [Talanta 233 (2021) 122598]. The biomarkers of immune system activation show great potential as a diagnostic tool for the monitoring general health, and they can facilitate monitoring of both disease progression and effects of therapeutic treatments [J. Periodontol. 73 (2002) 720–725]. The potential of salivary specific biological markers was investigated for oral, breast, pancreatic and prostate cancer; dementia; Alzheimer's disease; Parkinson's disease; hepatitis B [Metabolites 10 (2020) 47]. There are many properties of human saliva that make it an attractive diagnostic fluid. It can be easily, non-invasively and safely collected, reducing the discomfort and risk associated with invasive methods such as blood sampling [Int. J. Mol. Sci. 17 (2016) 846]. In the present study, a liquid chromatography-tandem mass spectrometry (LC-MS/MS) was developed for fast analysis of six kynurenine pathway metabolites in human saliva samples. Salivia samples were collected using the Salivette®, and metabolites were extracted using methanol-ethanol mixture. Separation and identification were performed by high-performance liquid chromatography coupled to triple quadrupole mass spectrometry (LC-TQ), electrospray ionization in positive mode (ESI+) was employed. A multi reaction monitoring (MRM) method was developed, which enabled determination of tryptophan, L-kynurenine, kynurenic acid, quinolinic acid, anthranilic acid and 3-hydroxyanthranilic acid.

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YP-60

Characterization of the aromatic profile of *Passiflora Edulis* Sims from Canary Islands (Spain) using solid-phase microextraction: A tool to discriminate new vegetive materials

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Keywords: *Passion fruit, Volatile organic compounds, Gas chromatography, Headspace solid-phase microextraction, Mass spectrometry*

Passion fruit is cultivated in warm and humid regions like South America, with an average temperature of 25 ºC. In the Canary Islands (Spain), the cultivation of this fruit is possible due to their climate conditions. As the consumption of this fruit is increasing worldwide, there is interest in having a genetically homogeneous material for its proper production and exploitation. Farmers are interested in cultivating passion fruits that can be adapted to grow in mild warm regions, while being drought and disease resistant, with good agronomic properties such as tutoring or pollination, and good organoleptic characteristics (odor and flavor).
The purpose of this study is to evaluate the organoleptic characteristics of passion fruits from Canary Islands, understood as a mixture of volatile organic compounds (VOCs) and non-volatile organic compounds (NVOCs), responsible of the flavor and the smell.
With respect to the volatile fraction, it depends on the fruit species and variety, the region where it was grown, and the degree of ripeness or the elaboration process, among others. Most tropical fruits are dominated by terpenes and esters in their volatile profile. In this case, the passion fruit is also known for its high content different esters (linear, branched, and substituted). Among this family, ethyl butanoate, ethyl hexanoate, and 2-methylbutyl hexanoate have been reported.
This study reports a headspace-solid-phase microextraction (HS-SPME) method in combination with gas chromatography-mass spectrometry (GC-MS) for the qualitative analysis of the volatile profile of tropical passion fruit juices. The optimization of the parameters affecting the HS-SPME method in the matrix is important to ensure success in monitoring VOCs in these fruit juices. This study selects several VOCs (mostly terpenes and esters) as target compounds, while optimizing the HS-SPME method with a Doehlert experimental design using a commercial SPME coating (CAR/PDMS). A total of 18 passion fruit samples were analyzed with the optimum method, and a factorial analysis (principal component analysis) was applied for the discrimination of different new materials of passion fruits.

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YP-61

LC-QTOF discovery of metabolomic markers for the quality control of sunflower and rapessed oils

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Keywords: *Plant oils, Metabolomic markers, Food authenticity, Liquid chromatography, Mass spectrometry*

Vegetable oils play an important role in the daily diet of people around the world and have gained significant popularity over animal-based fats, which is attributed to their nutritional properties [Toxins 11 (2019) 621]. Currently, vegetable oils account for more than 75% of all lipids consumed in the daily diet [Trends Food Sci. Technol. 74 (2018) 26–32]. The high consumption of vegetable oils is associated with the growing health awareness of the human population and the knowledge about bioactive compounds present in various oilseeds, such as: minerals, phytochemicals, vitamins and essential unsaturated fatty acids and their health-promoting properties [Sci. Rep. 10 (2020) 19971]. The richness of compounds present in vegetable oils depends on the plant species, region, cultivation method, water availability, and sunlight [Agric. Water Manage. 221 (2019) 150–159]. The method used to obtain vegetable oils is also important. The cold pressing method is currently the most widely used in the industry for the production of pharmaceutical oils, applying the temperature below 50 ºC allows to maintain the highest quality of healthy compounds in the final product [J. Am. Oil Chem. Soc. 87 (2010) 1497–1505]. Due to their high demand and short shelf life, cold-pressed oils reach high prices and are covetable commodities on the market, which makes them susceptible to adulteration [Food Anal. Methods 9 (2016) 712–723]. In most cases, fraud in the food industry consists of deliberately misleading consumers by mixing or substituting high quality products with lower quality products in order to gain financial benefits [Meat Sci. 173 (2021) 108374]. Therefore, to protect consumers, there is an urgent need to implement advanced analytical methods to detect adulteration of expensive cold-pressed oils from various oilseeds and oleaginous fruits [Sci. Rep. 10 (2020) 19971]. The aim of the study was to identify oil-specific metabolic markers to differentiate two vegetable oils (sunflower and rapeseed) from other types of edible oils. Liquid chromatography coupled to quadrupole time-of-flight mass spectrometry was used to analyse oil extracts. Here we present the primary results on the discovery of metabolic markers for the quality control of the sunflower and rapeseed oils.

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YP-62

Shotgun mass spectrometry for qualitative and quantitative assessment of lipidomic profiles of several edible oils

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Keywords: *Lipidomics, Mass spectrometry, Edible oils, Food authentication*

Every year, numerous of new products are introduced to the food market, which are made of very different, sometimes niche raw materials. To protect health and consumer rights, it is important that food control laboratories are able to provide reliable and rapid tests of the quality of these products and detection of possible adulterations. We propose fast and environmentally friendly method of analysis based on shotgun mass spectrometry to authenticate a few niche edible oils. The analysis is based on the fingerprints of selected lipid groups. As a result, complex lipid profiles of camelina (CA), flax (FL) and hemp (HP) seed oils were obtained.
By applying PCA (principal component analysis), it was possible to detect and distinguish each of them at different levels (diglycerides, triglycerides, group or combined). Lipid markers specific to the oils have also been identified, which may be used in targeted analyses. The obtained results may contribute to the improvement of existing or the development of new, comprehensive methods of authentication and detecting adulteration in edible oils.

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YP-63

Extraction and determination of curcumins and gingerols in ginger and turmeric nutraceuticals with validated UHPLC-DAD method

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Keywords: *Ultra-high performance liquid chromatography, Curcumin, Piperine, Gingerol, Food supplements*

The aim of the study was to develop and validate new UHPLC method for determination of gingerols and curcumins in nutraceuticals containing the extract of turmeric and ginger. These nutraceuticals are requested for their anti-inflammatory and antimicrobial effect, and it is desired to bring the information about their content. Developed and validated method was used for determination of gingerols, curcumins and piperine in following nutraceuticals: BIO Turmeric + Ginger – VANAVITA (GymBeam, s.r.o.), Kurkuma-Piperin (SETARIA), Kurkumin Advance (ADVANCE nutraceuticals, s.r.o.), Kurkumin-Piperin Plus (Vieste group, s.r.o.), Ginger Root Extract (SWANSON), Giner Root (SOLGAR), Ginger Root Extract (BIOMEDICAL), Kurkumin 550 mg (Jamieson laboratories), Shogaol Zázvor (EPIGEMIC), and Zázvor (VITOLIFE). The mixture of acetonitrile, methanol and acetic acid (38:60:2) was used for the extraction from samples of nutraceuticals. The solutions of samples were sonicated 10 minutes. Extracts were filtrated through 0.22 µm PTFE filters. The analysis was performed on the YMC Triart C_{18} ExRS (150 mm × 3.0 mm, 1.9 µm) chromatography column at the temperature of 35 °C. The gradient elution program was used, mobile phase consisted of acetonitrile and ultrapure water. The separation was performed at flow rate of 0.4 $mL \cdot min^{-1}$ and the detection was carried out using DAD detector at wavelength of 230 nm. Subsequently, the content of active substances in the preparations have been evaluated and the quality of individual food supplements have been compared. This research revealed that turmeric and ginger extracts are rich source of curcumin, gingerol, and their derivatives. However, the quality of the tested preparations in term of main analytes content differed according to the producer.

YP-64

On-line SPE-HPLC determination of ochratoxin A in ice and straw wine and phenolic compounds profiling

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Keywords: *Straw wine, Ice wine, Ochratoxin A, Phenolic compounds, On-line solid-phase extraction*

The presented study is focused on the complex characteristics of ice and straw wines, especially in terms of their benefits to the human body in the form of the antioxidant activity of phenolic compounds, and the analysis of risks associated with the presence of mycotoxins, specifically ochratoxin A. Production of ice wine, a special type of dessert wine, requires fully ripened grapes that are harvested and pressed at a temperature maximally -8 °C or below, resulting in a small amount of juice highly concentrated in sugars, acids, and aroma compounds [J. Sci. Food Agric. 84 (2004) 1675–1684]. Due to the special requirements, ice wine production is limited to only a few countries that meet those conditions during the winter; studied samples of ice wine, respectively straw wine, comes from vineyards of the Czech wine regions. The sweet dessert straw wine production entails grapes dehydration after harvesting, lasting 3 or 4 months. During the drying phase grapes lose most of the liquid, grapes lying in the sun or indoors on a rack or hanging in the air. [Food Chem. 305 (2020) 125512]. The result is very similar to that of the ice wine process, but the production of straw wine is more typical for warm climate countries.
More than twenty samples of straw and ice wine were evaluated in terms of phenolic compounds profile, including hydroxybenzoic and hydroxycinnamic acids, stilbenes, and flavan-3-ols. The 17 phenolic compounds were identified and quantified by a newly developed ultra-high performance liquid chromatography method with diode array detection. Further, due to the risks of mycotoxin contamination during the harvest and processing of both wines, the analytical method involving online SPE coupled to HPLC-FD using column switching was developed to monitor the ochratoxin A. The results of the investigation of ochratoxin A contamination in ice and straw wines were compared with the European Union maximum tolerable limit of 2 µg/L.

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YP-65

Development and application of an organo-silica membrane functionalised with amino groups for the determination of macrolide antibiotics in eggs

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Keywords: *Macrolide antibiotics, Eggs, Organo-silica membrane, Liquid chromatography, Mass spectrometry*

Macrolides are a group of high-spectrum antibiotics used over the years to treat respiratory and intestinal infections in livestock and poultry, given that they are effective against a wide range of bacteria, including gram-positive and some gram-negative bacteria. These antibiotics can be obtained from various organisms of the genus *Streptomyces*. They are characterized by a large macrolactone ring containing 14, 15 and 16 carbon atoms. Some of the most commonly used are erythromycin, spiramycin, and tylosin, among others. The use of these substances can lead to health problems such as gastrointestinal dysfunction, cochlear nerve damage, nephrotoxicity, ototoxicity, resistance, etc., when they are used incorrectly or excessively. Sometimes if withdrawal times are not adequate in animals they can appear as residues in some foods such as milk, meat, eggs, etc. The EU Commission Regulation 37/210 establishes maximum residue limits for these antibiotics in different foods of animal origin, such as egg, milk, liver, kidney, etc. For this reason, the control of these residues is needed, and sometimes the methodologies are not able to reach the detection limits required by legislation. In addition to the fact that the matrices in which these residues are found are very complex, requiring extraction and preconcentration techniques. For this reason, the aim of this work was to synthesise an organo-silica membrane functionalised with amino groups to purify 5 macrolide antibiotics (spiramycin, erythromycin, josamycin, roxithromycin and tylosin) from chicken egg extracts prior to analysis by liquid chromatography coupled to mass spectrometry. The membrane was synthesised in several steps and characterised by elemental analysis, nitrogen physisorption and scanning electron microscopy. Once the membrane was synthesised and characterised, it was placed in a holder and coupled to a solid-phase extraction vacuum box and the typical SPE stages were checked. For this purpose, different loading solvents (acetonitrile (ACN), water, water 0.1% formic acid, water/ACN (90/10, v/v), water/ethanol (90/10, v/v)) and elution solvents (methanol (MeOH), ACN, MeOH 1% acetic acid, MeOH 1% ammonia) were tested using standard solutions at 100 ng/g, assessing the membrane behaviour towards target analytes. The best conditions were loading the standard solutions in water and eluting with MeOH and MeOH with 1% ammonia. Once the best loading and elution solvent was selected, a Box-Behnken design of experiments was used to optimize the purification conditions in the egg extract previously obtained with 2.5 mL ACN in 1 g of a mixed egg. The design experiment was a 3-variable, 3-level experiment to optimise the loading volume, the elution volume and the amount of ammonia used in the elution solvent (MeOH). Within the experimental design optimised conditions, the methodology was fully validated, showing good accuracy, good linearity, and adequate precision. The methodology was then successfully applied to egg samples. The membranes can be reused more than 100 times and were kept undisturbed for 4 years.

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YP-66

Monofloral honey analysis using vacuum assisted HS-SPME

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Keywords: *Monofloral honey, Solid-phase microextraction, Vacuum*

The development and use of a gas chromatography-mass spectrometry (GC-MS) approach combined with vacuum-assisted headspace solid-phase microextraction (vac-HS-SPME) for the analysis of monofloral honey types are presented in this thesis. The honey types under investigation include buckwheat, sweet clover, alhagi, and sunflower.

The research emphasizes the benefits of vac-HS-SPME over traditional HS-SPME approaches in addition to fiber setting. By encouraging the release of volatile chemicals from the honey samples, vacuum assistance improves the extraction efficiency and increases the sensitivity and accuracy of the analysis.

Accurately identifying the honey's botanical source is one of the biggest hurdles in honey analysis since different floral sources provide the finished product different chemical compositions and sensory qualities. The distinct flavor characteristics and potential health advantages of monofloral honeys.

To address this analytical challenge, various techniques have been developed to differentiate monofloral honeys based on their chemical profiles. The combination of HS-SPME and GC-MS has proven to be one of these methods' most effective means of examining volatile chemicals in honey. While GC-MS enables their separation and identification based on their mass spectra, HS-SPME allows the selective extraction and concentration of volatile chemicals present in the headspace above a sample.

Vac-HS-SPME has attracted a lot of attention recently since it has the potential to increase extraction efficiency and sensitivity in comparison with conventional HS-SPME procedures. This method offers enhanced analytical performance, and reduced analysis time compared to conventional techniques. In this thesis, we aim to develop and optimize a Vac-HS-SPME coupled to GC-MS method to differentiate buckwheat, sweet clover, alhagi, and sunflower honey types.

The first objective of the research is to determine the most effective fiber type for extracting target analytes from the monofloral honeys. To obtain the highest extraction efficiency, three fiber types, namely blue, grey, and pink, coated with a DVB/CAR/PDMS (divinylbenzene, carboxen and polydimethylsiloxane), combination, will be conducted to achieve the best extraction efficiency.

In addition to fiber optimization, the study focuses on optimizing the extraction time and temperature to enhance the efficiency of the HS-SPME technique. The parameters of time and temperature play a crucial role in the extraction of volatile compounds from the honey samples, and their optimization can significantly improve the sensitivity and accuracy of the analysis.

The results show that among all honey types, the grey fiber exhibits the highest extraction efficiency for most of the target analytes. However, when extracted using the blue fiber as opposed to the pink and grey fibers, some substances, including butanoic acid, 3-hydroxy-3-methyl, 3-(N-abncetyl-N-methylamino) propionic acid, and butanoic acid, 2,2-dimethyl-, methyl ester, exhibit much greater peak areas. In comparison to the pink and blue fibers, the grey fiber exhibits marginally superior extraction efficiency for the chemical nonanoic acid in buckwheat honey. In addition, compared to the other fiber types, grey fiber removes a greater amount of chemicals (totaling 16 compounds).

Moreover, the utilization of vacuum-assisted HS-SPME offers distinct advantages over conventional HS-SPME, including enhanced extraction efficiency and improved analytical performance. The optimized parameters of extraction time (30 minutes) and temperature (60 ºC) contribute to the overall efficiency of the analysis.

The study helps to improve the HS-SPME approach for honey analysis and offers insightful information for monofloral honey quality control and authenticity assessment. Furthermore, the method may have broader applications in the analysis of other food products requiring precise differentiation based on volatile profiles.

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YP-67

Optimization of a solid-phase microextraction gas chromatography-mass spectrometry method for volatile profiling of aromatized extra virgin olive oils

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Keywords: *Aromatized extra virgin olive oil, Solid-phase microextraction, Volatiles, Gas chromatography-mass spectrometry*

The consumption of extra virgin olive oil (EVOO), exclusively obtained by mechanical or physical processes from the fruits of olive trees, is generally accepted to provide many beneficial effects on human health (antioxidant, anti-inflammatory, cardioprotective, anti-tumor, etc.) [Foods 9 (2020) 1014; Agriculture 13 (2023) 993]. These properties have been described to be associated with its high content of fatty acids and other minor components (phenolics, sterols, tocopherols, etc). Moreover, the unique aroma of EVOO originating from complex mixtures of volatiles also plays an important role, not only when identification of sensorial defects is intended, but also to determine consumer preference. In an attempt to diversify the market and to provide consumers with products with improved organoleptic properties, EVOOs naturally aromatized with a number of plant and spice matrices (aEVOOS) have recently been commercialised. However, the characterization of the volatile composition of these products has so far been scarcely addressed [Food Chem. 202 (2016) 221–228; Molecules 24 (2019) 2625].

In this study, a new method by solid-phase microextraction (SPME) has been optimised for volatile profiling of aEVOOs obtained by malaxation of olives (*Olea europaea* Ottobratica) harvested in Reggio Calabria (Italy) and different aromatic matrices [bergamot (*Citrus bergamia*) fruit, turmeric (*Curcuma longa*) spice, ginger (*Zingiber officinale*) root and mace (*Myristica fragrans*) spice]. First, evaluation of different SPME fiber coatings was carried out. The 2-cm divinylbenzene/carboxen/polydimethylsiloxane SPME fiber was chosen as optimal as it provided an improved overall recovery of aEVOO volatiles. Miniaturization of the SPME procedure by selecting 0.1 mL of aEVOO as sample volume and selection of the most appropriate internal standard (tridecane) for quantitation was also done. A 3-level factorial experimental design, considering as experimental factors the extraction temperature (T, in the range 40-60 °C) and time (t, 20-60 min) was used for optimization of the SPME procedure. A multiple response considering maximization of volatiles exerting a positive influence on aroma (*cis*-3-hexenal, 2-hexen-1-ol, 1-penten-3-one, hexan-1-ol and *trans*-2-hexenal), and the minimal extraction of volatiles previously described as bad or undesirable notes (heptanal, 2-heptenal, octanal and 2,4-heptadienal) was considered in the selection of the optimal SPME operating conditions. Moreover, other chromatographic parameters such as the splitless time and the oven temperature programme were also individually optimized for the different samples here studied.

Under optimal SPME conditions (T = 44 °C, t = 60 min), a total of 79-130 volatiles were identified/characterized in the four aEVOOs analysed. Aliphatic alcohols, aldehydes and esters were the most predominant chemical classes arising from olive oil. Moreover, characteristic volatile terpenoids from the matrix used for EVOO aromatization (e.g. bergamol in bergamot aEVOO; zingiberene in ginger aEVOO; etc.) were also detected by SPME GC-MS. Regarding quantitation, *trans*-2-hexenal (a marker of Calabrian EVOOs) (0.06-0.25 mg·mL^{-1}), limonene (0.004-3.32 mg·mL^{-1}), *β*-pinene (0.0001-0.34 mg·mL^{-1}), α-pinene (0.001-0.3 mg·mL^{-1}), etc., were some of the major aEVOO volatile compounds.

In conclusion, SPME followed by GC-MS is shown as an affordable, fast and solvent-free technique which can be performed with low sample amount and be easily implemented at the food industry for characterization of the aroma of added-value aEVOOs.

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YP-68

Application of liquid-liquid extraction for LC/MS-based authentication of camelina seed oil

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Keywords: *Cold-pressed oils, Lipidomic profile, Authenticity*

Oil adulteration is a worldwide and continuing issue, especially for nontraditional plant oils pressed from fruit seeds. These oils are sources of natural biologically active substances which provide excellent health-promoting properties [J. Food Compos. Anal. 107 (2022) 104373]. In case of adulteration with other cheaper oil, the high quality could be degraded, while the most typical indicators, such as color and consistency are maintained. The purity of oil could be proven using a wide variety of analytical methods. High-performance liquid chromatography (HPLC) coupled to mass spectrometry (MS) is one of the most frequently used analytical technique for oil adulteration detection [Methods Mol. Biol. 708 (2011) 247–257]. Camelina (*Camelina sativa* L.) is an annual plant that originated in eastern Europe and western Asia. Oil derived from the seeds of the plant contains mainly unsaturated fatty acids (linoleic and γ -linolenic acids) and large amounts of tocopherols. The well-balanced fatty acid profile confer favourable nutritional benefits, preventing coronary heart disease and many inflammatory conditions. The presence of sterols and tocopherols ensure strong antioxidant activity, reducing LDL levels in blood serum [Food Control 130 (2021) 108349]. The aim of the study was to detect lipid features characteristic for cold-pressed camelina seed oil and to differentiate it from unrefined sunflower oil. A liquid-liquid extraction method was used to isolate the lipids from the oils. Analysis was conducted by high-performance liquid chromatography coupled to high-resolution quadrupole time-of-flight mass spectrometry (LC-QTOF 6500 Agilent Technologies). Lipidomic profiling was performed using Mass Profiler Professional (Agilent Technologies). The application of this method allowed to distinguish the two tested oils.

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YP-69

LC-MS profiling of gluten extracts from model bread dough supplemented with phenolic acids

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Keywords: *Gluten structure, Phenolic acid, Mass spectrometry*

Health-conscious nutrition is nowadays very important aspect for people all over the world. One of the key component of the human diet is wheat bread. The quality of the bread dough is crucial and can be affected by the structural/storage proteins gliadins and glutenins. These proteins form continuous viscoelastic network within dough called 'gluten' [J. Cereal Sci. 108 (2022) 103570], that has a complicated structure related to the type of wheat and how it is processed. Supplementing bread with compounds that may have positive effects on health is an adequate way to enrich diet. Additives include polyphenol extracts or dietary fiber from by-products of antioxidant (polyphenols) rich foods. The most common group of plant phenolic compounds are phenolic acids, which are also natural antioxidants. Due to their anticoagulant, anti-inflammatory properties they can help prevent cardiovascular diseases, cancer and diabetes [J. Mol. Struct. 1246 (2021) 131219]. Therefore, addition of phenolic acids during dough mixing can bring strong benefits and improve health. However, it can also disrupt formation of the gluten network by reducing its strength, further increasing elasticity and thus, may influence the sensory quality of bread [J. Sci. Food Agric. 89 (2009) 2356–2363]. Recent data suggests that there is an incorporation of phenolic acids into gluten network during dough mixing process [Food Chem. 389 (2022) 133109], yet the mechanism of these interactions is not fully understood. In this study, gluten extracts from model dough samples, supplemented with various phenolic acids, were subjected to proteomic analysis. Liquid chromatography coupled with high-resolution mass spectrometry (LC-QTOF-MS) technique was used. Obtained proteomic profiles were next evaluated at QUAL/QUANT level.

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YP-70

Ultrasound-assisted extraction, purification by solid-phase extraction with sulfonic acid-functionalized SBA-15 and HPLC-MS/MS analysis for the quantification of opium alkaloids in ground poppy seeds

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Keywords: *Opium alkaloids, Ground poppy seeds, Ultrasound-assisted extraction, Solid-phase extraction, Food safety*

In recent years, there has been an increasing trend to add different types of seeds to food for their good nutritional properties, one of them being poppy seeds, which come from *Papaver somniferum* L. (or commonly opium poppy plant). These seeds are usually ground for use in traditional sweet dishes and cakes, especially in Central Europe. It can also be sprinkled on bread rolls and added to sauces such as in many curry mixes or for thick sauces. However, it has been found that these seeds may be contaminated with opium alkaloids (OAs) due to contamination with the proper latex of the plant. Consumption in high concentrations can lead to severe cases of intoxication and even false positive drug tests. Therefore, a maximum limit of morphine equivalents (morphine + 0.2 x codeine) of 20 mg/kg has been established. However, it has been found that seeds can be contaminated with high concentrations of other OAs (thebaine, papaverine, noscapine, and oripavine) and that these can be even more toxic. For this reason, health authorities are demanding further studies taking into account all the main OAs to establish real exposure and the legislation accordingly. To date, there is not an optimised and validated analytical method to analyse ground seeds. For this reason, the aim of the present work was to develop and validate an efficient, rapid and as environmentally friendly as possible methodology for the quantification of the six main OAs in ground poppy seeds by liquid chromatography coupled to a triple quadrupole tandem mass detector (HPLC-TQ-MS/MS). To do this, firstly, the ultrasound-assisted extraction (UAE) step was optimised using design of experiments, considering three factors at three levels (3^3) such as solvent (methanol, water and ethanol), solid/solvent ratio (0.5 g/3 mL, 0.5 g/5 mL and 0.5 g/10 mL) and extraction time (3, 5 and 10 min). Besides, the greenness of the proposed method was evaluated according to AGREEprep, which is a new metric tool focusing on sample preparation. The results showed that it could be considered a greener analysis than using classical magnetic stirring. This is because complete extraction of OAs was achieved using a lower sample/solvent ratio and shorter times, showing that the implementation of UAE is more environmentally friendly, approaching closer to Green Analytical Chemistry (GAC). Subsequently, a purification step by solid-phase extraction (SPE) was optimised to eliminate possible matrix effects that can cause incorrect results and further deterioration of the equipment. For this purpose, a previously synthesised material of SBA-15 silica functionalised with sulfonic groups (SBA-15-SO3-) was used, and the conditions of the purification steps (conditioning, loading and elution) were optimised to achieve adequate recovery values with only 25 mg of material. Finally, this methodology was adequately validated in terms of linearity, the limits of detection and quantification were low enough to be able to correctly detect and quantify OAs concentrations in ground poppy seed samples. Furthermore, accuracy and precision were performed at three concentration levels based on the maximum limit set by legislation (low level: 3.4 mg/kg, medium level: 20 mg/kg and high level: 40 mg/kg) and mean recovery values between 85 and 100% were obtained for all analytes and inter-day and intra-day precision were below 15% in all cases. In addition, selectivity was also properly evaluated by comparing retention times and fragment ion intensity between standards and samples. Finally, the developed methodology was successfully applied to the analysis of OAs in different types of ground poppy seeds obtaining, in some cases, concentrations higher than those established by legislation, which highlights the need to analyse these types of samples in order to minimize public health problems.

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YP-71

Evaluation of new ferrofluidic materials for the extraction of chiral pesticides from environmental water, followed by enantioselective liquid chromatography analysis coupled with tandem mass spectrometry

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Keywords: *Ferrofluid, Pesticides, Enantioseparation, Green solvents, Magnetic nanoparticles*

Ferrofluids (FFs) are quite stable colloidal dispersions of nanometer-sized magnetic particles suspended in a carrier liquid. The intriguing tunable magnetic properties of these materials and their liquid nature have spread their use in various fields of science, ranging from medicine to magneto-chemistry, and, recently, they have been employed as extraction materials in magnetically assisted analytical sample preparation procedures. FF-based extraction takes advantage of both the magnetic susceptibility of nanoparticles and the properties of the liquid carrier, which are responsible for a wide variety of interactions with analytes and for the extraction performance [Separations 8 (2021) 47]. Among the most appealing aspects of ferrofluids systems, there are the greenness and the simplification of the sample preparation procedures since time-consuming steps such as centrifugation and the use of expensive equipment are not necessary [Talanta 160 (2016) 340–346]. The magnetic nanoparticles must be stabilized in a carrier liquid which acts as an extractant to avoid agglomeration due to Van der Waals forces, by resorting to a coverage strategy.
In this work, five chiral pesticides were extracted with a liquid-phase microextraction technique based on the use of a ferrofluidic material. Two different fatty acids were tested as coverages for the magnetic nanoparticles, and the extraction power of three green solvents was investigated. Current trends in analytical chemistry are looking for the replacement of toxic organic solvents in many microextraction methods with safer alternatives [Curr. Opin. Green Sustain. Chem. 18 (2019) 13–19]. In particular, this work investigated the use -as carriers- of eutectic solvents from renewable and natural sources, inspired by their recent applications in pesticide analysis in wines [Molecules 27 (2022) 908], but also the employment of low-cost, non-toxic fruit esters. In fact, both of these neoteric solvent categories are making their way into the world of microextraction, and recently, precisely a fruit ester has been successfully applied to the extraction of pesticides from urine, an unquestionably complex aqueous-based matrix [J. Pharm. Biomed. Anal. 223 (2023) 115150]. The extraction procedure was coupled with the development of an enantioselective LC-MS/MS method for the enantioseparation and quantification of the selected analytes from environmental water samples, using a polysaccharide-based chiral stationary phase. To date, extensive treatment of crops with racemic agrochemicals leads to wide enantiomeric pollution, the so-called “isomeric ballast”, that can not only harm aquatic life but can potentially cause health problems in humans [Food Chem. 277 (2019) 298–306]. In fact, stereoisomers of agrochemicals not only show different efficiency and toxicity towards the target and non-target species but undergo biological transformations at different rates [Biodegradation - Life of Science, Chapter 10 (2013) 251–287]. In order to investigate the possible exposure to different isomers of pesticides as well as their spread in the environment, the development of chiral separation methods is evermore an urgent necessity. After validation, the method here presented was successfully applied to extract and quantify the chiral pesticide residues in local river water.

YP-72

Copper and nickel preconcentration by a dispersive liquid-liquid microextraction method using a hydrophobic deep eutectic solvent

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Keywords: *Microextraction, Deep eutectic solvent, Metal determination*

The increasing awareness and concern for the environmental protection has led to the incorporation of green chemistry principles in different chemical processes, including those involved in the analytical methodologies. In this context, it is crucial to thoroughly evaluate analytical procedures to assess their potential environmental impact and found alternative approaches to mitigate them. Current research is focus on the use of green solvents such as deep eutectic solvents (DESs) which have gained significant attention as sustainable extraction media. DESs are non-toxic, environmentally friendly, inexpensive, and easy to prepare solvents usually composed of two molecules, a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), that form a homogeneous liquid when mixed at a certain temperature. The wide variety of HBA and HBD combinations enables the design and synthesis of DES with hydrophobic or hydrophilic characteristics, or DES that can acts as both, extraction solvent and chelating agent, allowing the extraction of metals through the formation of the complex.

The aim of this work is the development of a green and simple dispersive liquid-liquid microextraction method using DES for the determination of copper (Cu) and nickel (Ni) in water samples. To achieve this aim, hydrophobic DESs based on water-insoluble substances (such as menthol or thymol) and nonpolar fatty acids (such as capric acid or lauric acid) were investigated as chelating agent and extraction media for the simultaneous preconcentration of both elements. The effect of pH of the sample, sample volume to DES volume ratio, mixing time, centrifugation time, temperature, and salt concentration on the extraction efficiency were evaluated. Under optimal conditions, the extraction efficiency for Cu and Ni were about 95 and 70%, respectively. The principal analytical figures of merit of the method such as preconcetration factors and precision were estimated, and the applicability of the method was evaluated in different water samples.

YP-73

Efficiency of natural deep eutectic solvents to extract phenolic compounds from tea samples by a micro-ultrasonic-assisted extraction

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Keywords: *Natural deep eutectic solvents, Polyphenols, Tea, Micro-ultrasonic-assisted extraction*

Natural deep eutectic solvents (NADESs) have recently emerged as a promised alternative to conventional solvents since they present several advantages such as their biodegradability, low cost, high stability and low toxicity. NADESs are composed of natural components (primary metabolites) such as sugars, alcohols, amino acids, organic acids, and choline derivatives, and at a specific molar ratio composition, they present a significant melting point depression, becoming liquids [ACS Sustain. Chem. Eng. 2 (2014) 1063–1071]. Thus, NADESs are suitable for the development of new sample treatments aligned with the green sample preparation principles [Trac–Trends Anal. Chem. 148 (2022) 116530], and currently, they are having a special interest for the extraction of biologically active compounds from natural sources.

In this regard, in this study we propose the extraction of phenolic compounds from tea samples using NADES as extraction solvent in a micro-ultrasonic-assisted extraction (micro-UAE) prior to their determination by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). The chromatographic separation of 22 phenolic compounds was performed on a Zorbax HD, C_{18}, (2.1 x 100 mm,1.8 µm) employing water with 0.1% formic acid and methanol as mobile phases. The MS operated in both positive (ESI+) and negative (ESI-) electrospray ionization modes and polarity, and all the compounds were analysed under multiple reaction monitoring (MRM) conditions selecting two ion transitions for each compound.

A selection of 11 different NADESs composed by choline chloride, lactic acid, citric acid, glycerol, glucose and fructose were prepared at different ratios using the heating and stirring method. The composition of the NADESs and their corresponding molar ratio was as follows: citric acid:glycerol:water (1:1:3), citric acid:fructose:water (1:1:5), lactic acid:fructose:water (5:1:3), lactic acid:glycerol:water (1:1:3), lactic acid:glucose:water (5:1:9), lactic acid:glucose:water (5:1:3), choline chloride:fructose:water (2:1:1), choline chloride:citric acid:water (1:1:5), lactic acid:choline chloride:water (3:1:3), choline chloride:glucose:water (1:1:5) and choline chloride:glycerol:water (1:2:6). All these mixtures were analysed by nuclear magnetic resonance (NMR) spectroscopy to confirm the formation of the supramolecular structure by the presence of nuclear overhauser effect (NOE) in the 1H NMR spectra of each NADES. Afterwards, the extraction efficiency of these solvents was evaluated, using 100 mg of dried green tea sample and 1 mL of each NADES. Then, 100 µL of the supernatant was redisolved in ethanol:water (50:50, v/v) for its injection into the LC-MS/MS system. In addition, the results were compared with those obtained by using a traditional extraction solvent composed by ethanol:water (70:30, v/v). The best extraction, in terms of the highest signal for the target phenolic compounds, was achieved when lactic acid:glycerol:water (1:1:3) was used as extraction solvent. The main compounds found in green tea were gallocatechin, epigallocatechin gallate, epicatechin, catechin, epicatechin gallate, rutin, isoquercetin, among others. In order to optimize the micro-UAE, the key parameters influencing the extraction efficiency were investigated and optimized by the response surface methodology (RSM) based on a central composite design (CCD). The three variables included in this design were: plant/solvent ratio (from 30 to 100 mg), temperature (from 20 to 50 °C), and extraction time (from 10 to 30 min). The optimal conditions were then selected for the characterization of the method in terms of linearity, limits of detection and quantification, precision and matrix effects. Finally, the characterized method was used for the determination of phenolic compounds in green, black and red tea samples from the supermarket.

To sum up, in this work we have demonstrated the phenolic extraction capacity of different NADESs which were characterized for the first time. Moreover, a micro-UAE using lactic acid:glycerol:water (1:1:3) has been presented as a greener alternative to the traditional extraction procedures used so far.

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YP-74

Optimization of natural deep eutectic solvent-microwave-assisted extraction of birch (*Betula* sp.) bark bioactives

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Keywords: *Birch (Betula sp.) bark byproducts, Microwave-assisted extraction, Natural deep eutectic solvents, Betulin, Betulinic acid*

Revalorization of forest byproducts as a source of high-value bioactives is nowadays considered as an ecosustainable and profitable activity. Among other natural sources, the large quantities of birch (*Betula* sp.) bark produced from wood processing make this biomass a source worthy of exploration. Moreover, birch bark is rich in lupane-type triterpenoids (e.g. betulin (Bet) and betulinic acid (BAc)) for which a wide variety of bioactivities (anti-inflammatory, antibacterial, antimalarial, antidiabetic, anti-HIV, anticancer, etc.) have been described [Phytochem. Rev. 18 (2019) 929–951].

Advanced extraction techniques such as microwave-assisted extraction (MAE) have been shown to overcome conventional solid-liquid extraction (SLE) methods in terms of extraction yield and time, solvent volume required, etc. for a number of applications regarding the extraction of bioactives from vegetable sources [Plants 9 (2020) 392; J. Chromatogr. A 1635 (2021) 461770]. Whereas conventional organic solvents are generally employed to this aim, their replacement by using greener and affordable alternatives such as natural deep eutectic solvents (NADESs) in combination with MAE has not been previously addressed for the enhanced extraction of birch bark bioactives.

In this study, optimization of a MAE method by using as extractant a hydrophobic NADES (thymol:1-octanol, 4:1 molar ratio), previously reported as optimal for the extraction of birch bark bioactives [Luque-Jurado et al., EuSP 2022 Conference], has been done by means of a 3-level factorial experimental design. Experimental factors to be evaluated were temperature (T) (40-80 °C) and time (t) (5-30 min). Optimal MAE conditions, monitored by using a reverse phase-liquid chromatography-mass spectrometry ((RP)LC-MS) method, were selected to maximize the recovery (in $mg \cdot g^{-1}$ dry sample) of individual bioactives (Bet and BAc). Moreover, a multiple response aimed to the simultaneous maximization of both responses was also considered. After validation in terms of precision and accuracy, this MAE method was further applied to six different commercial birch bark samples.

Under optimized conditions, MAE provided an improved and shorter extraction of birch bark bioactives over SLE. A wide variability with the sample considered was also found regarding Bet and BAc contents of MAE extracts. In conclusion, MAE in combination with NADES is shown as an efficient and green approach for the extraction of bioactive birch bark triterpenoids within a biorefinery frame.

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YP-75

Comparison of microwave-assisted extraction and subcritical water extraction to obtain anti-aging extracts from a brewer's waste

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Keywords: *Microwave-assisted extraction, Subcritical water extraction, Barley malt rootlets, Anti-aging*

The agri-food industry generates a large amount of by-products. Mainly used as animal feed, agro-industrial waste has attracted attention as a source of bioactive compounds with potential applications in many sectors such as food, cosmetic, nutraceutical, pharmaceutical, and packaging [Front. Biosci. 28 (2023) 3]. This strategy would bring economic and environmental benefits, turning the food industry into a sustainable and environmentally friendly production system that promotes a circular and sustainable economy [Food Chem. 370 (2022) 131315].
Barley malt rootlets (BMR) are a waste from the brewing industry containing a high amount of proteins and phenolic compounds, among other bioactive substances [Trends Food Sci. Technol. 127 (2022) 181–197]. The exploitation of this waste requires the development of methodologies with low environmental impact. Previous works of our research group evaluated the potential of pressurized liquid extraction and ultrasound-assisted extraction to recover proteins and phenolic compounds from BMR observing the high potential of this waste to obtain highly antioxidant extracts [Curr. Res. Food Sci. 5 (2022) 1777–1787].
This work proposes to evaluate the potential of microwave-assisted extraction (MAE) and subcritical water extraction (SWE) for the recovery of extracts with anti-aging power from BMR under sustainable conditions. In both cases, water was used as extracting solvent while the temperature and extraction time were the optimized variables. The optimization was aimed at obtaining extracts with a high capacity to scavenge ABTS radicals and to inhibit different enzymes involved in aging (elastase, collagenase, hyaluronidase and tyrosinase). The content in proteins and phenolic compounds of extracts was also monitored. Since these properties were promoted at high extraction temperatures, a subsequent study of the formation of Maillard products, with undesirable effects, was also carried out. Higher antioxidant properties were observed when using subcritical water extraction. These properties were enhanced at higher extraction temperature but limited by the formation of Maillard products. Overall results suggested the potential of both sustainable techniques for obtaining extracts from BMR with promising properties for the cosmetic industry.

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YP-76

Optimization of green extraction techniques for determination of bisphenols in human breast milk samples via HPLC-FLD

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Keywords: *Dispersive liquid-liquid microextraction, High-performance liquid chromatography, Fluorescence detector, Bisphenols, Human breast milk samples*

Bisphenol A (BPA) is one of the most produced chemical worldwide, and it is ubiquitous in everyday life. Its omnipresence combined with toxicity led authorities throughout the world to put limits on its use in food contact products and totally banned it in products for infants like feeding bottles and nipples. It led to the introduction of the production of BPA substitutes, which are often other bisphenols (BPs) such as, bisphenol S (BPS), bisphenol F (BPF), bisphenol AF (BPAF), bisphenol E (BPE). Unfortunately, these compounds are suspected of being similar or even more toxic than BPA. Moreover, apart from BPA, BPS and BPA diglicydyl ethers (BADGEs), these compounds are not currently under any restrictions. In addition, the metabolism is less effective in infants, and it is mainly based on conjugation with the glucuronic and the sulfuric acid of free forms of BPs to safer, conjugated forms. Human breast milk is commonly the main source of food at the early stage of life. It makes infants one of the most vulnerable groups for exposure to these analytes, especially in its free forms. Considering these facts, the constant development of methods for biomonitoring large number of bisphenols simultaneously appears to be crucial.
Interesting technique which was successfully applied for BPs analysis in human breast milk is dispersive liquid-liquid microextraction (DLLME). DLLME was firstly developed in 2006 by Assaidi and co-workers for isolating poliaromatic hydrocarbons from water samples [J. Chromatogr. A 1116 (2006) 1–9]. DLLME extraction technique for determination of 7 bisphenols in human breast milk samples with high-performance liquid chromatography coupled with fluorescence detector (HPLC-FLD) was successfully optimized. The method was used for the determination of 7 bisphenols in 10 human breast milk samples [Molecules 28 (2023) 1432]. The method was further optimized to improve the greenness. To lower the usage of harmful solvents, vortex-assisted liquid-liquid microextraction (VA-LLME) was performed. In comparison to DLLME, VA-LLME does not contain dispersive solvent. An extracting solvent or mixture of solvents are directly added to the aqueous sample. Similarly to the DLLME, extracting solvent must not be miscible with water. During optimization of the VA-LLME procedure, the two different extracting solvents were tried: dichloromethane (DCM) and trichloromethane (TCM) and DCM:TCM 1:1 (v/v). The optimization of the extraction solvent or mixture volume has started from 1 mL. The 0.5 mL of a human breast milk sample in a polypropylene tube has been diluted to 5 mL with water. Then the extraction mixture has been added, and the tube has been mixed thoroughly for 1 min. Tubes were centrifuged, and the lower layer has been withdrawn and evaporated to dryness. Residues have been reconstituted with 300 µL of acetonitrile:water 1:1 v/v and analyzed via HPLC-FLD.
Microextraction techniques like DLLME or VA-LLME have provided satisfactory method parameters. They do not need any sophisticated or energy consuming laboratory equipment. Finally, the DLLME and the VA-LLME have been compared using AGREE model [Anal. Chem. 92 (2020) 10076–10082] with other popular extraction techniques (QuEChERS, SPE) and found to be more environmentally friendly.
High-performance liquid chromatography coupled with fluorescence detector might be an interesting alternative to the most popular techniques used in biomonitoring of bisphenols like LC-MS and GC-MS. Its sensitivity achieved by signal amplification have provided competitive limit of detection (LOD) and limit of quantification (LOQ) values below 1 ng/mL [Molecules 28 (2023) 1432] during bisphenols analysis. Additionally, thanks to selectivity of FLD, the matrix components signal were low which resulted in reliable analysis. Presented methods are dedicated for analyzing free forms of bisphenols. For analyzing the total level of bisphenols additional enzyme hydrolysis step with β-glucuronidase/sulfatase should be added prior to extraction. However, considering the toxicity of free forms for infants and the impact of its exposure on the later life, the determination of free forms was found to be specifically relevant.

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YP-77

Cellulosic supports modified with beeswax for the determination of tricyclic antidepressants

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Keywords: *Cellulose, Beeswax, Antidepressants*

Sample treatment cannot be omitted in most analytical processes; therefore, it has been adapted to the principles of green chemistry. To minimize its impact on the environment, several measures have been incorporated in these procedures, such as the integration of the number of stages, the automation of the analytical process, the reduction of energy and solvent use, and the reduction of waste generated, among others. The use of paper in the development of sorptive phases for sample treatment has been a growing trend in the scientific community. Due to its biodegradable nature, reduced cost and easy coupling to numerous analytical techniques, many studies in microextraction lean toward the use of this material. Paper has been used both unmodified and modified with different sorbent phases. This project focuses on the second modality, more specifically on the modification through physical deposition.

Supports based on paper modified with wax of natural origin (i.e., beeswax) have been developed, following the principles of green analytical chemistry on the use of biodegradable materials. Unmodified paper has hydrophilic character. Although it can be used as sorbent phase, its modification with wax widens its range of application, turning it into a hydrophobic material capable of extracting non-polar compounds.

Cellulosic supports have been modified by coating filter paper with beeswax using three synthesis techniques: dip-coating and two modes of drop-casting. Dip-coating consists of immersing the paper in melted wax, followed by air-drying. For the synthesis using the drop-casting method, two modalities have been considered: a) the deposition of a controlled volume of melted wax over the paper and b) the deposition of a specific volume of wax previously dissolved in a solvent (hexane). The characterization of the material has been carried out by ATR-IR and SEM to confirm the presence of the coating on the paper, as well as the uniformity of the surface after the synthesis. SEM images of the modified paper showed that the lattice formed by the cellulose fibers is covered by wax, showing different degrees of thickness depending on the synthesis method used. From the study of the spectra obtained by ATR-IR, this coating of the paper is confirmed by the presence of bands corresponding to the aliphatic chain and the ester groups of wax. Of the three syntheses, the drop-casting method based on the dissolution of the wax in hexane shows remarkable properties compared to the others. The deposition of the wax by this method, together with the evaporation of the solvent, creates a thin coating on the paper, preserving its porosity, as well as providing it with the hydrophobic properties of wax.

The modified paper has been used for the extraction of tricyclic antidepressants (TCAs) in aqueous samples to determine its capacity as a sorbent. The variables affecting both the synthesis of the material and the extraction process were optimized using high-performance liquid chromatography. To test the efficiency of the support as a sorbent phase, the material was subjected to an extraction process, being incubated in aqueous standards of a mixture of TCAs (500 µg/L). The high recovery percentages (up to 70%) confirm the viability of these supports as sorptive phases in the extraction of non-polar contaminants.

Regarding the optimization of the process, the variables have been divided depending on whether they affect the synthesis of the material or the extraction. In relation to the variables affecting the synthesis, intermediate values of 150 µL and 12.5 g/L of volume deposited and concentration of wax were chosen, respectively. The optimum value for pH was selected at 10.5. As for the extraction, 30 min was adopted for the incubation time, with a stirring speed of 1000 rpm. The study of the ionic strength confirms that the presence of salts does not significantly affect the process at NaCl values below 0.5% (m/v).

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YP-78

Fabric phase sorptive extraction followed by gas chromatography and tandem mass spectrometry for the simultaneous determination of 12 synthetic musks in water

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Keywords: *Fabric phase sorptive extraction, Synthetic musks, Gas chromatography, Tandem mass spectrometry, Environmental water*

Synthetic musks are a class of synthetic fragrances additives which are employed in personal care products (cosmetics) and household products (e.g. detergents) with the purpose of creating pleasant scents and making products more attractive to consumers. However, because of their toxicity, estrogenic imbalance and carcinogenecity, they are considered emerging pollutants and their presence in some environmental compartments (water, soil, air) is mainly because of sewage systems. According to their chemical structure, these fragrances can be classified in polycyclic, nitro, macrocyclic and alicyclic musks, being three of the studied nitro musks in this investigation banned in cosmetic products due to the nitroaromatic group they have in their structure [Adv. Mar. Biol. 81 (2018) 213–280].
The aim of this work is the development of an analytical methodology able to determine simultaneously trace levels of 12 synthetic musks, including nitro (musk xylene, musk ambrette, musk moskene, musk tibetene, musk ketone), polycyclic (galaxolide, celestolide, phantolide, cashmeran, traseolide, tonalide) and macrocyclic musk (ambrettolide), in real environmental water. The methodology is based on fabric phase sorptive extraction as the sample preparation, followed by gas chromatography-tandem mass spectrometry (FPSE-GC-MS/MS). An asymmetric screening experimental design was done optimizing the influence of nine factors on FPSE sample preparation. The factors included the sol-gel sorbent coating, stirring mode, extraction time, desorption time, salting-out effect, sample volume and type and volume of desorption solvent. Under optimized conditions, the proposed method was validated considering linearity ($R^2 \geq 0.9904$), repeatability (RSD < 6%), reproducibility (RSD < 12%) and accuracy (75-120%), showing satisfactory results in all these terms. Finally, the validated methodology was applied to real water samples (seawater, river water, wastewater, laundry water, etc.), showing the presence of 11 out of the 12 target synthetic musks, including the three banned nitro musks.

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YP-79

The use of ionic liquids for the separation of clinically relevant biogenic amines by the MEKC method from urine sample

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Keywords: *Ionic liquids, Metanephrines, Biogenic amines, Micellar electrokinetic chromatography, Neuroblastoma*

In recent years, attempts have been made to design and create alternative solvents for traditional organic solvents. Due to the unique and diverse properties, ionic liquids (ILs) are an interesting alternative. Actually, ILs are receiving more attention in various fields of analytical chemistry. The literature date confirms their contribution to the enhancement of the extraction, clean-up, separation and determination of trace amounts of various biologically important compounds in distinct matrices. Furthermore, imidazole-based ILs, can be used to prevent the sorption of the analyzed compounds onto the capillary walls. In this research, I focused on the determination of biogenic amines (BAs). BAs are organic compounds that act as neurotransmitters and they are important due to the number of physiological functions they perform in the human body. Moreover, BAs are involved in the most common pathologies for human diseases. Therefore, determination of their concentration is important and helpful in the diagnosis of complex and varied types of cancer, such as phaeochromocytoma, neuroblastoma (NBL) and other catecholamine-secreting tumors [Talanta 238 (2022) 122997; Separations 10 (2023) 116].

The research consisted of two stages. Firstly, evaluation of the influence of ILs as a background electrolyte (BGE) component as flow modifiers in the micellar electrokinetic chromatography (MEKC) analysis of selected BAs. Specifically, the experiments focused on 12 ILs containing a cation consisting of an imidazole ring with different alkyl substituents and anions. Besides, one tested ILs contained a pyridinium cation. This stage of research concerned: the critical evaluation of the effects of imidazolium-based ionic ILs on the separation efficiency of selected BAs and their metabolites, such as vanillinmandelic acid (VMA), homovanillic acid (HVA), 3-methoxy-4-hydroxyphenyl glycol (MHPG), dihydroxyphenylglycol (DHPG), normetanephrine (NM), methanephrine (M), dihydroxyphenylacetic acid (DOPAC) during MEKC analysis [Talanta 238 (2022) 122997]. Coating the capillary wall with a cation layer increases its surface stability, consequently improving the repeatability of the separation process. The results showed that the most effective ILs added to the BGE were those with a chloride anion and tetrafluoroborate anion [Talanta 238 (2022) 122997].

Further studies will focus on complete validation of the methodology for the MEKC analysis of BAs with the use of selected imidazolium-based ILs, and the optimized method will be next applied for the analysis of real samples obtained from oncology patients with disturbances in the level of BAs. In this step, MEKC is employed to evaluate how two ILs with different anions, namely [$HMIM^+Cl^-$] and [$HMIM^+BF_4^-$] affect the separation efficiency for biogenic amines, such as M, NM, VMA, and HVA in urine samples. The validation data confirmed the method's linearity (R^2>0.996) for all analytes within the range of 0.25-10 µg/mL. The applicability of the optimized SPE-MEKC-UV method was confirmed by employing it to quantify clinically relevant BAs in real urine samples from pediatric neuroblastoma (NBL) patients. The relative standard deviations (RSD) of the migration times achieved with [$HMIM^+Cl^-$] were lower than IL with anion BF_4^-.Therefore, [$HMIM^+Cl^-$] was used to modify the inner wall of the capillary during the validation step and for the determination of the selected BAs in real urine samples. The obtained validation results confirmed that the proposed SPE-MECK method satisfies the criteria for bioanalytical method validation recommended by FDA and ICH guidelines. The proposed IL-modified MEKC method was applied for the analysis of real urine samples from eight pediatric patients with NBL [Separations 10 (2023) 116].

These findings clearly demonstrate the usefulness of [$HMIM^+Cl^-$] in the analysis of VMA, HVA, M, and NM in urine samples. Moreover, all the results relating to the use of ILs enabled the development of an analytical method for the determination of BAs in urine samples. Finally, the concentration levels measured for the tested analytes (significantly elevated for M and NM, and a low VMA/HVA ratio) proved the necessity of monitoring BAs in biofluids from cancer patients and provided new data for use in future clinical and pharmacokinetic studies.

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YP-80

Determination of polychlorinated biphenyls (PCBs) and polychlorodibenzo-p-dioxines (PCDDs) in baby diapers employing natural deep eutectic solvents

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Keywords: *Deep eutectic solvents, Endocrine disrupting chemicals, Diapers, Gas chromatography-mass spectrometry*

In this work a new method involving solvent extraction of porous membrane-packed solid samples (SE-PMSS) coupled to GC-MS has been developed for the determination of six polychlorinated biphenyls (PCBs) and five polychlorodibenzo-p-dioxines (PCDDs) in disposable baby diapers. In that aim, a terpenoid-based natural deep eutectic solvent (NADES) composed of carvone and camphor in a 1:1 molar ratio was used. The extraction process consisted on a first sealing step of the homogenized whole diaper inside a polypropylene bag. The bag was immersed in a proper amount of NADES and agitate. After that, measurements were carried out injecting the NADES with the extracted analytes directly into the GC-MS system. Previously, a Box-Behnken experimental design was performed to know the optimum variables of the extraction process. Under optimized extraction conditions, the method was validated obtaining good analytical features such as low limits of detection (0.1-0.8 µg/g) and quantification (0.2-2.8 µg/g). Relative recoveries ranged between 85 and 120% and relative standard deviations (RSDs) under 15% for all the analytes. Finally, the green character of the developed method was evaluated employing ComplexGAPI and AGREEprep tools. As far as we know, this is the first time that deep eutectic solvents, and more specifically NADESs, have been employed for SE-PMSS and for the analysis of baby diapers.

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YP-81

Supported liquid-solid-phase extraction using wetted nanofiber discs as a simple approach for extraction of water contaminants

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Keywords: *Nanofiber discs, Polymer-based nanofibers, Supported liquid extraction, Chlorophenols*

Polymer-based nanofibers have become a hot trend in new extraction sorbent development. These sorbents are rather hydrophobic with higher affinity toward lipophilic analytes. Addition of small amount of octanol onto the discs right before the extraction is a new, simple approach to increase the nanofibers affinity toward moderate-lipophilic analytes. Novel supported liquid-solid-phase extraction (SL-SPE) approach was tested to extract 9 common pesticides, insecticides, and plasticizers (p-nitrophenol; 2-; 4-; 2,5-; 2,4,6-; 2,3,4,6-chloro-phenol; bisphenol A; permethrin and fenoxycarb) with wide range of log P values (1.9–6.5). Three different nanofibrous polymers (polyacrylonitrile PAN, poly hydroxybutyrate PHB and polylactic acid PLA) were chosen as a sorptive phases. Nanofiber mats were fabricated by alternating current electrospinning technique and cut into small discs. Extraction experiments were conducted in a beaker, with nanofiber discs attached to a metal rod as a home-made spinning device. After the extraction, desorption was made in one-step, directly in HPLC vial. This approach eliminates time consuming evaporation and reconstitution steps, commonly featured in SPE protocols. Addition of only 50 µL octanol on the nanofiber discs resulted with even 5-fold increase in analyte's peak areas when compared to native discs. Highest enrichment factors were observed for analytes within the 3.3-4.5 log P range. Analytes with higher log P (permethrin log P 6.5) were extracted better with native discs. Differences between the three tested polymers with and without octanol's addition were observed and compared. The effect of sample volume, disc diameter, disc mass, and time of extraction was evaluated. Promising preliminary experiments encourage more thorough research. Further optimization of the influence of the sample pH, ionic strength, desorption conditions and octanol's amount as well as extraction from real matrix will be discussed.

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YP-82

Enhanced extraction of bisphenol analogues in environmental waters using automated systems in combination with 3D-printed millifluidic devices containing metal-organic frameworks and molecularly imprinted polymers

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Keywords: *Metal-organic frameworks, Molecularly imprinted polymer, Bisphenols, Solid-phase extraction, 3D-printing*

The use of 3D-printing technology has experienced a significant increase in recent years due to its ability to effortlessly design and print tailored systems at an affordable price. Specifically, stereolithography (SLA) 3D-printing mode allows printing with high layer resolution and high-quality surfaces, providing final objects that are chemically compatible with organic solvents, and thus offer many opportunities in the analytical chemistry field. However, 3D-printed devices designed for sample preparation are limited in terms of surface area and selectivity; yet, the easy surface modification of the 3D-printed devices allows its combination with sorbent materials, thus boosting their potential for the development of applications for sample preparation. In this regard, the combination of 3D-printed devices with molecularly imprinted polymers (MIPs), which provide selective interactions, is an appealing marriage to improve 3D-printing features. Nevertheless, despite several limitations on the MIP use, including limited interaction sites and low mass transfer, MIPs have recently been synthetized onto metal-organic frameworks (MOFs), which has proven to surpass these constraints.
In this study, a 3D-printed millifluidic device containing a MOF-MIP sorbent has been fabricated for the extraction of an important group of emerging pollutants in environmental water samples: bisphenol analogues (BPA, BPS BPC, BP-AP and BP-AF). These compounds are of concern in the environment since they affect the wildlife and are highly mobile, thus easily incorporate into the food chain. The aforementioned device has been designed with a coiled tubular channel configuration inside of which the MOF-MIP composite was successfully immobilized. The MIP was prepared for BPA, although it is supposed to also act as a dummy template for the other bisphenols. Furthermore, the retention potential of the MOF-MIP combination for these analytes was compared against the MIP alone, the MOF alone, non-imprinted polymer (NIP) and the combination MOF-NIP. The extraction conditions have been also optimized and the figures of the merit of the method have been also established. Additionally, the 3D-printed device has been connected to a sequential injection analysis setup to fully automate the extraction procedure as a front end to on-line HPLC-FLD/DAD for the detection and quantification of the target bisphenols in environmental waters.

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YP-83

3D-printed devices and molecularly imprinted polymers for riboflavin extraction and detection in food samples: A smartphone-based colorimetric sensor

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Keywords: *Sensing, Molecularly imprinted polymer, Riboflavin, Smartphones, 3D-printing*

Riboflavin (vitamin B2) is an essential vitamin in the human diet and plays an important role in cellular growth, development and function, as well as energy production from food. This component is present in certain foods such as milk, eggs or organ meats and it is also available as dietary supplement. Due to its health importance, it is necessary to evaluate the daily intake and its presence in food. Hence, the development of fast, simple and sensitive methodologies for its analysis is important nowadays. Within this context, and considering that the compound has a very characteristic yellowish coloration, the use of methods based on smartphone-based sensors is proposed as a very interesting and accessible alternative for the detection of the vitamin. By combining the advantages of molecularly imprinted polymers (MIPs) and 3D-printing, it becomes possible to create customized devices that exhibit selective retention for riboflavin, enabling subsequent sensing using a smartphone. This innovative approach offers several advantages, including affordability, and ease of use. The MIPs used in this sensor are synthetic receptors that are specifically designed to recognize and bind to riboflavin molecules with high affinity and selectivity enhancing the sensitivity of the material compared with conventional porous organic polymers. On the other side, the 3D-printing technology allows for the precise fabrication of tailored structures, enabling the integration of these MIPs into the smartphone sensor. The third part of this system is the smartphone camera that uses colorimetric detection, where the presence and concentration of riboflavin are determined based on changes in color intensity. In this study, a colorimetric assay for the detection of riboflavin is conducted using a smartphone's camera as detection device. For this, solid-phase extraction performance is carried out using a 3D-printed cartridge designed with a flat surface to simplify the use of the smartphone's camera. The detection and quantification of the compound can be directly determined analyzing RGB intensity parameters of the smartphone photos with an image software (*Image J*). For this purpose, the cartridge is filled with the sorbent materials for the extraction of the analyte using non-imprinted polymers (NIP) or the selective extraction using then MIP with riboflavin as a molecular template. The MIP has shown improved detection and quantification values in calibration curves. Moreover, the 3D-printed devices favored the detection of the analyte, compared to conventional solid-phase extraction columns, which are completely cylindrical. Overall, this innovative combination of smartphone-based sensors, molecularly imprinted polymers, and 3D-printing technology presents a promising avenue for the fast and reliable analysis of riboflavin in food samples, providing an easy and cost-effective solution.

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YP-84

Evaluation of natural deep eutectic solvents for the selective extraction and stability enhancement of bioactive compounds from saffron (*Crocus sativus*)

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Keywords: *Natural deep eutectic solvents, Saffron (Crocus sativus), Crocins, Safranal, Bioactive compounds stability*

In the last decade, there has been increasing interest in the extraction of bioactive compounds from plants for their use in different formulations in food and cosmetics industry. Among the sources of bioactive compounds, saffron (*Crocus sativus*) is a valued spice with several bioactives, mainly picrocrocin, safranal, crocins and kaempferol derivatives [Phytochemistry 162 (2019) 56–89]. However, the different chemical structures of these bioactives make their selective extraction, either for their analysis or for the production of supplements or ingredients, a major challenge. Nowadays, natural deep eutectic solvents (NADESs) are being evaluated as promising solvents because of their ability to tune their selectivity depending on their composition and their biodegradable nature. Moreover, NADESs have shown the ability to stabilize certain bioactive compounds that are unstable in other solvents [Food Chem. 159 (2014) 116–121].

Therefore, the main objective of this work was to evaluate, for the first time, the possibility of using NADESs for the selective and enhanced extraction of saffron bioactive compounds compared to that of classical solvents (methanol/water). Moreover, the ability of these NADESs to stabilize these bioactives was also evaluated. To that aim, two hydrophilic NADESs (based on choline chloride as hydrogen bond acceptor) and three hydrophobic NADESs (based on thymol as hydrogen bond acceptor) were synthesized. Then, the extraction of grounded saffron stigmas was carried out using NADES or a methanol:water mixture (50:50, v/v) under mechanical agitation at different temperatures (30 and 45 ºC). Diluted extracts were analyzed by HPLC-DAD-MS and the extracts were kept in the fridge for one month for stability study.

As expected, different extracting capacity was observed depending on the hydrophilic or the hydrophobic character of the NADES used. While both hydrophilic solvents (choline chloride:ethylene glycol and choline chloride:glycerol) were able to extract picrocrocin, safranal, crocins and kaempferol derivatives in similar concentrations to that for hydroalcoholic solvent, thymol-based NADES showed a lower extraction capacity for these bioactives. The length of the hydrocarbon chain of the acids used as bond donor for the thymol-based NADES affected significantly to the solubility of crocins, picrocrocin and kaempferols, with the highest solubility values being obtained with butyric acid and the lowest with decanoic acid. However, safranal was the only compound that practically was unaffected by the acid considered.

These results show the promising potential of hydrophilic NADES as a sustainable and green alternative to organic solvents for the extraction of bioactives from saffron to be used as food ingredients or nutraceuticals.

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YP-85

Ionic liquid-based thin-film membranes supported on plastics and cellulose paper for phenols removal from water

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Keywords: *Ionic liquids, Thin-film solid-phase microextraction, Removal, Phenols, High-performance liquid chromatography*

Ionic liquids (ILs) are solvents with melting temperatures below 100 °C and entirely composed by ions. The most common IL cations are derived from ammonium, phosphonium, imidazolium and, guanidinium. Commonly used anions are halides, such as chloride or bromide, or more complex structures, like hexafluorophosphate and tetrafluoroborate. Their main characteristics include great tunable capacity, negligible vapor pressure at room temperature, low flammability, modulable viscosity and solubility, and an impressive solvation capacity for a variety of compounds. Several subclasses of ILs have been developed in the last years. Among them, metal containing-ILs (MCILs) contain at least a metal component in their structure, whereas polymeric ionic liquids (PILs) are polymers prepared from an IL acting as monomer. Both MCILs and PILs possess some of the advantages of ILs, together with other features derived from their metallic and polymeric characters, respectively.
In analytical microextraction, ILs and MCILs have been widely used in dispersive liquid-liquid microextraction (DLLME) and/or single-drop microextraction (SDME), whereas PILs have been extensively used in solid-phase microextraction in the fibers format (SPME). Thus, there is the need of exploring new microextration modes together with these materials.
Among microextraction techniques, thin-film solid-phase microextraction (TF-SPME) involved the use of a thin layer of extraction material. This format allows for increasing the amount of material used for extraction and its surface area, compared to in fiber SPME, but without the inconvenience of increasing the extraction time as the thickness coating is thin (ensuring fast diffusion of analytes). In any case, the incorporation of liquid materials in TF-SPME devices is not common, being the supported liquid membranes (SLMs) the most usual ones.
The objective of this work is to obtain TF-SPME devices based on ILs, MCILs, and/or PILs supported on polystyrene, PTFE and/or cellulose paper. The preparation and characterization of these devices was performed. As proof of concept, the devices were applied for the removal of phenols in combination with high-performance liquid chromatography and diode array detection.

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YP-86

In-situ growth of metal-organic frameworks onto braid silver fibers as novel devices for solid-phase microextraction

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Keywords: *Solid-phase microextraction, Metal-organic frameworks, Braid silver fibers, Persistent organic pollutants, Environmental analysis*

Solid-phase microextraction (SPME) has become an indispensable tool in analytical chemistry laboratories due its outstanding preconcentration capability and simplicity. Conventional SPME consists of a capillary support, generally a fused silica wire or a metallic core, coated with a polymeric material in a micro syringe-like configuration. Over the last years, researchers have focused their attention on the modification of the classical SPME design by either the incorporation of new materials with novel properties, or by using novel supports with interesting surface chemistry. Novel materials constitute an alternative to conventional polymers, that present as main drawbacks their relatively low selectivity and low thermal and chemical stability. Among the novel materials implemented in SPME, metal-organic frameworks (MOFs) should be highlighted. MOFs are well-defined materials composed by metallic centers coordinated with organic ligands, building highly porous frameworks. MOFs present unique physicochemical properties, including the highest known surface area due to their impressive internal cavity system, high thermal and chemical stability due to its inorganic nature, and high tuneability. Therefore, MOFs have been proposed as designed materials for different analytical sample preparation techniques, including SPME.
With respect to modifications of supports in SPME, several alternative supports have been proposed over the last decade to overcome disadvantages of silica, mostly metallic wires (metallic alloys as stainless steel or nitinol). Nevertheless, these metallic wires are generally difficult to functionalize if intending to attach alternative coatings on them. Thus, novel wires with much more superficial reactivity have been studied, like silver. Silver wires can be functionalized via thiol chemistry while involving fast, mild, and reproducible procedures. At the same time, silver wires are flexible, property that can be exploited to generate braided supports that can be incorporated in the current SPME design, allowing an increase in robustness and a considerable upgrade in the amount of coating available to interact with analytes during the extraction process.
In this sense, this work presents the novel incorporation of MOFs and silver braided supports in SPME. Different MOF-SPME fibers were prepared by mild functionalization of the silver braid support with mercaptoacetic acid and subsequently a direct *in-situ* growth of MOF crystals onto the supports. These devices were tested for the determination of different families of hydrocarbons as representative examples of persistent organic pollutants. The overall methodology involved headspace SPME coupled with gas chromatography tandem mass spectrometry. Besides, commercially available fibers were also tested and compared for the same application.

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YP-87

Green extraction of phenolic compounds from olive leaves: Investigating deep eutectic solvents

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Keywords: *Polyphenols, Olive leaves, Natural deep eutectic solvent, Extraction, High-performance liquid chromatography-tandem mass spectrometry*

Agri-food industries generate a large amount of waste that offers great revalorization opportunities within the circular economy framework. In the case of the oil production industry, olive leaves are a by-product and an important source of antioxidants. Phenolic compounds are one of the most important families of secondary metabolites in plants. These compounds have antioxidant, anti-inflammatory, and antimicrobial properties, and for these reasons have been linked to positive effects on diseases such as cancer, diabetes, hypertension, and cardiovascular diseases, among others. In recent years, new methodologies for the extraction of compounds with more eco-friendly solvents are being developed, such as the case of natural deep eutectic solvents (NADESs).
In this study, a methodology for the extraction of phenolic compounds with NADESs is optimized. The solvent components (combinations of glycerol, urea, and lactic acid with choline chloride), the molar ratio between them, the percentage of water, and the conditions of temperature and extraction time were optimized. The extracts obtained were analyzed by HPLC-MS/MS with MRM mode. The conditions established as optimal for olive leaves rely on a solvent composed of choline chloride and glycerol at a molar ratio of 1:5 with 30% water, at 80 ºC for 2 h with constant agitation. Comparison with conventional ethanol/water extraction has shown that NADES improved extraction efficiency as well as being a more environmentally friendly alternative. The main polyphenols identified in choline chloride and glycerol extract were luteolin-7-glucoside (262 $mg \cdot kg^{-1}$ fw), oleuropein (174 $mg \cdot kg^{-1}$ fw), 3-hydroxytyrosol (129 $mg \cdot kg^{-1}$ fw), rutin (33 $mg \cdot kg^{-1}$ fw) and luteolin (27 $mg \cdot kg^{-1}$ fw).

YP-88

Polyphenols recovery from natural deep eutectic solvent extracts using polymeric resins: Searching strategies for sustainable extraction

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Keywords: *Phenolic compounds, Polymeric resins, Olive leaf, Agro-food waste valorization, Circular bioeconomy*

Polyphenols, a huge group of chemical compounds naturally present in fruits, vegetables, cereals, nuts, etc., have attracted significant attention due to their potential health benefits attributed to their antioxidant and anti-inflammatory properties. These compounds have been associated with protective effects against cardiovascular and neurodegenerative processes, as well as a reduction in the risk of certain types of cancer.
The agro-food industry sector generates substantial volumes of waste that are rich in phenolic compounds, providing a valuable opportunity to recover polyphenols in line with the principles of the circular bioeconomy approach. Moreover, employing natural deep eutectic solvents (NADESs) for polyphenols extraction enhances the sustainability of the process, which adds a greener dimension to the overall strategy.
In this study, we present column experiments using MN202, PAD900, and LW S 7968 polymeric resins for the recovery of polyphenols from NADES olive leaf extracts. The adsorption process is performed at the natural pH of the extract, while elution is carried out using ethanol-water mixtures under various pH conditions.
This research shows the potential of polymeric resins in facilitating the recovery of polyphenols from NADES extracts, highlighting their suitability for this application.

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YP-89

Metal-organic frameworks as solid-phase sorbents in different formats for the isolation of synthetic cannabinoids in oral fluids

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Keywords: *Drugs, Paper-based devices, Cartridge, Solid-phase extraction*

Analytical chemistry has recently evolved towards a new concept of chemistry, being of special relevance the greenness developed analytical methodologies. For instance, portability, reduction of reagent consumption, waste generation, miniaturization, easy-to-use, etc. are highly desirable. In this sense, the use of smart materials able to quantitatively retain analytes with a very low amount of sorbent could lead to the development of new methods to address modern problems including complex matrices, analytes at trace levels or high level of interferents. Bearing in mind the White Analytical Chemistry (WAC) principles [Trac–Trends Anal. Chem. 138 (2021) 116223], an analytical procedure was developed for the isolation of synthetic cannabinoids (SCs) in oral fluids by using (micro)solid-phase extraction devices with metal-organic frameworks (MOFs) as sorbents. After the optimization of parameters (such as MOF nature, solvent composition and so on), the best candidate was the amino functionalized University of Oslo material (NH_2-UiO-66) and it was able to successfully retain 8 different SCs (67-114%) in oral fluids, with low RSD values (<11%) and limit of detection (LOD) as low as 0.6-0.8 $\mu g \cdot L^{-1}$ [Anal. Chim. Acta 1246 (2023) 340887]. On the basis of these previous results, a new concept of paper-based device (µPAD) has also been developed combining the benefits of cellulose platform and the rich chemistry of NH_2-UiO-66. The resulting composite, named as NH_2-UiO-66@paper, was fully characterized and the findings confirmed that the material was stable at both aqueous medium and under high temperatures. For these reasons, it was applied as portable extractive phase for SCs in aqueous matrices and their subsequently determination by ion mobility spectrometry (IMS). The method was optimized and provided adequate precision values in both intra- and inter-devices (RSD < 12%), good accuracy (recoveries around 54-116%) and the limit LOD was down to 10 ng using a portable system. Furthermore, the NH_2-UiO-66@paper can perfectly be used with screening purposes instead of using sophisticated and non-portable systems.

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YP-90

Pillared-layer CIM metal-organic frameworks: Improved strategies for analytical microextraction

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Keywords: *Pillared-layer metal-organic frameworks, Canary Islands materials, Dispersive micro-solid-phase extraction, Personal care products*

Porous materials are key sorbents in analytical microextraction strategies. Among them, metal-organic frameworks (MOFs) have brought considerable interest, given their outstanding properties. MOFs are highly ordered crystalline structures with impressive surface areas, high porosity, and tunability linked not only to the variety of combinations metal clusters and ligands in their structure but also for their ability to experience post-modifications. In this context, these properties and their potential analytical exploitation have always been strongly dependent on the precursor agents used (metal centers and organic ligands) and the conditions applied for the proper synthesis of these reticular materials. Its correct selection has allowed controlling their geometry, functionality, and porosity, by promoting the establishment of specific coordination bonds and desirable interactions with target compounds. As a result, attention is beginning to be drawn toward the employment of mixed-component MOFs, such as pillared-layer MOFs [Coord. Chem. Rev. 451 (2022) 214273]. Pillared-layer MOFs are a subclass of MOFs based on their rational design and construction through mixed-ligand synthetic procedures, where different types of ligands are used to obtain a more complex framework that may offer pore size/shape diversity. In turn, it is expected an improvement in the sorption capacity for different target analytes present in a variety of samples, and, in particular, better desorption features when using organic solvents as desorption agents in microextraction.
In this study, a new set of Zn-based pillared-layer MOFs from the Canary Islands Materials (CIM) family is presented. The proposed CIM MOFs were evaluated as alternative sorbents in dispersive micro-solid-phase extraction combined with high-performance liquid chromatography and diode array detection, for the determination of a group of personal care products. Besides, their performance is compared with the already reported CIM-81(Zn) MOF, which also presents a pillared-layer structure [Molecules 24 (2019) 690; ACS Appl. Mater. Interfaces 13 (2021) 45639–45650].

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YP-91

Mixed-matrix membranes based on a metal-organic framework and recycled polystyrene and their use in thin-film microextraction for the determination of personal care products

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Keywords: *Thin-film microextraction, Metal-organic framework, Recycled polystyrene, Mixed-matrix membrane, Personal care products*

Metal-organic frameworks (MOFs) are crystalline solids consisting of inorganic metal ions or metal clusters and organic ligands linked by strong coordination bonds. Their main characteristics depend on the selected organic ligands and their connectivity in the structure, together with their porosity, particle size, and nature of the metal cluster, among other factors. MOFs are considered an ideal extraction material due to their high surface area and also to their great versatility, as the number of possible metal-ligand combinations is almost infinite. Their combination with other materials such as magnetic nanoparticles, ionic liquids, or polymers, involves the formation of a composite with improved characteristics when compared with the neat MOF. In this aspect, it is important to highlight polymers, due to their high capacity to act as a binder to adhere the MOF to different supports.
In this work, it is used a composite formed by a MOF and recycled polystyrene (PS) obtained from yogurt plastic containers, with cellulose sheets as support to form a mixed matrix-membrane (MMM). The MMM was then used in thin-film microextraction (TF-SPME) for the determination of seven personal care products in different samples. The optimal MMM device involved a 30% w/v on load of the MOF MIL-100(Fe) and 5 layers, using a support size of rectangular shape (1.5 × 2.5 cm). The device could be reused more than 10 times without losing extraction efficiency. The type of extraction (static or dynamic), the extraction time, and the desorption solvent, time and volume, were optimized in combination with a high-performance liquid chromatograph coupled to a photodiode array detector. The results confirmed that the best desorption solvent was acetonitrile, and the extraction mode was dynamic, thus obtaining the best results in the shortest possible time. The final optimal conditions were obtained using an experimental design.
The samples under study were micellar waters from well-known brands and swimming pool waters from different places of Tenerife, Canary Islands. Quality analytical parameters of the calibrations in the samples included detection limits down to 2.5 $\mu g \cdot L^{-1}$ and relative standard deviations ranging between 2 and 26% using different batches of the MMMs and an intra/inter-day precision in triplicate at two levels of concentration (100 and 350 $\mu g \cdot L^{-1}$).

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YP-92

Metal-organic frameworks in matrix solid-phase dispersion for the extraction of phytochemicals from *Cannabis sativa* L. samples

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Keywords: *Cannabis sativa L., Matrix solid-phase dispersion, Metal-organic frameworks, High-performance liquid chromatography, CIM-80(Al)*

Fiber-type *Cannabis sativa* L. is a plant species known for its easy cultivation and rich phytocomplex, which mainly includes terpenoids, non-psychotomimetic cannabinoids, and flavonoids. These compounds are well-known for their health benefits for human health, including antioxidant, anti-inflammatory, and calming effect. For these reasons, this crop is now the subject of renewed interest in many fields such as pharmaceutical and nutraceuticals, among others.
Due to the high complexity of this plant, sample preparation is normally necessary to make the sample compatible with downstream analysis. Different approaches have been developed to extract and isolate bioactive compounds from *Cannabis sativa* L. matrices. These methods normally are tedious, involve time-consuming sample preparation steps, and require the consumption of large amount of organic solvent to extract the analytes of interest. To limit the use of toxic solvents and streamline the overall process, it is crucial to develop more sustainable and efficient methods for the extraction of natural compounds.
Metal-organic frameworks (MOFs) are a class of crystalline materials composed of metal ions connected by organic ligands through coordination bonds. These materials are characterized by the presence of accessible cages, tunnels and modifiable pores, and exhibit the highest known surface areas. Due to their impressive features, together with their versatility, MOFs have gained significant attention in different scientific field, including sample preparation. In this field, MOFs are employed sorbents in different procedures, including solid-phase extraction and different modes of solid-phase microextraction.
In this study, we propose the use of MOFs as sorbents in matrix solid-phase dispersion (MSPD) to extract non-volatile phytochemicals from different *Cannabis sativa* L. samples. This technique consists in the direct mechanical blending of the sample (usually a solid) with a solid sorbent, which allows to clean-up and homogenize the matrix.
Different MOFs have been tested as sorbents, being the MOFs CIM-80(Al) selected for its higher capacity to efficiently extract both flavonoids and cannabinoids from *Cannabis sativa* L. samples. Several experimental conditions (amount of sorbent and desorption step) were optimized using an experimental design to obtain the maximum extraction efficiency. In comparison to traditional extraction approaches, the resulting methodology is easier, quicker, and more environmentally friendly while keeping the requirements in terms of sensitivity for the target analytes.

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PVC-diphenilamine covalent bonding supported on cellulose for opioids extraction from saliva samples

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Keywords: *Cellulose, Polyvinyl chloride, Thin-film microextraction, Direct infusion mass spectrometry, Opioids*

In this work, the potential of cellulose paper as a substrate for preparing planar sorptive phases has been evaluated. These phases are sustainable and biodegradable, and they can be used in thin-film microextraction (TFME) due to their flat format. In this communication, the dip-coating technique is used to coat the filter paper with polyvinyl chloride (PVC), followed by the covalent bonding of diphenylamine by nucleophilic substitution. This technique consists of introducing the paper into a polymer solution, followed by solvent evaporation. Thus, a thin PVC coating is created on the paper surface, in which diphenylamine is linked by the same dipping-drying process. As a result, aromatic rings are available on the paper surface to isolate the target analytes by π- π interactions. The planar sorbent phase has been characterized using different techniques, such as infrared spectroscopy, UV-visible spectroscopy, and others qualitative tests. To evaluate the sorption capacity of modified paper, some opioids (codeine, methadone, and tramadol) are proposed as model analytes, which have been quantified using direct infusion mass spectrometry (DI-MS). Although unmodified paper contributes to the extraction of the analytes, the results show that the paper modification increases the extraction selectivity and sensitivity. In order to increase the amount of extractant while maintaining the porosity of the paper, some percentages of PVC and diphenylamine solutions are combined in the modification procedure to select the most efficient sorptive phase. To break the analyte-sorbent phase interaction, two different eluents have been evaluated: methanol, and methanol/formic acid (99/1 v/v). Different variables related to the extraction procedure have been studied, such as stirring rate, sample pH, and extraction time. Finally, the analytical performance has been evaluated in aqueous medium by DI-MS in terms of linearity, sensitivity, precision, and accuracy.

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