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2024 CHANIA CRETE GREECE

EuSP2024
3rd European Sample Preparation Conference

GSAC2024
2nd Green and Sustainable Analytical Chemistry Conference

15–18 SEPTEMBER 2024 · CHANIA · CRETE · GREECE

BOOK OF ABSTRACTS

www.eusp-gsac2024.tuc.gr

Title
Book of Abstracts – 3rd European Sample Preparation Conference and 2nd Green and Sustainable Analytical Chemistry Conference

Editor
Elefteria Psillakis

ISBN: 978-618-5558-09-3

Place
Chania-Crete, Grecce

Date
18 September 2024

Chair

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Welcome

Dear Participants,

On behalf of the Organizing Committee, it is a distinct pleasure to cordially welcome you to the 3rd European Sample Preparation Conference (EuSP2024) and the 2nd Green and Sustainable Analytical Chemistry Conference (GSAC2024), held simultaneously in Chania, Crete, Greece, from the 15th to the 18th of September 2024. These events are recognized by EuChemS and supported by EuChemS-DAC and the EuChemS-DAC Sample Preparation Study Group and Network.

EuSP2024 and GSAC2024 build on the success of the virtual events organized by the EuChemS-DAC Sample Preparation Study Group and Network in 2021 and 2022. The EuSP2024 | GSAC2024 program showcases innovative research, cutting-edge technology, and new products and techniques across a broad range of analytical and applied areas in sample preparation and green analytical chemistry. The list of plenary, keynote, and invited speakers includes internationally renowned experts whose contributions to sample preparation and green analytical chemistry have been outstanding. The key theme of the joint events is “Innovation,” aligning with the 2024 annual theme of the EuChemS-DAC Sample Preparation Study Group and Network. To commemorate this theme, the “EuSP2024|GSAC2024 Young Innovator Award” is launched. The best oral communication and three posters by young researchers will also be selected by an international jury and awarded for their outstanding research, thanks to support from our sponsors. A pre-conference course supported by the IUPAC project 2021-015-2-500 will focus on the greenness evaluation of sample preparation methods by AGREEprep and is open to all registered participants of EuSP2024 | GSAC2024. Two satellite workshops are also offered to all attendees thanks to support from our sponsors.

All participants are invited to submit a full-length manuscript for possible publication in a Special Issue dedicated to EuSP2024 | GSAC2024, organized in “Advances in Sample Preparation” (SAMPRE) by Elsevier. This dynamic journal, directly linked to the EuChemS-DAC Sample Preparation Study Group and Network, was recently awarded an Impact Factor of 5.2 (IF=5.2) by Clarivate Analytics in the 2024 Journal Citation Reports (JCR 2024) and was ranked as a Q1 journal.

This is the first time that the island of Crete, one of the most attractive travel destinations in Greece, hosts EuSP2024 | GSAC2024. The symposium will take place in the Center of Mediterranean Architecture and the “Mikis Theodorakis Theater Hall,” two adjacent, iconic, and historical monuments featuring contemporary architectural interventions that will provide an inspiring backdrop to the meeting. The conference venue, in the heart of the Venetian port in Chania, surrounded by monuments dating back to 5000 BC, provides the perfect setting for us to interact, collaborate, exchange ideas, and work towards a brighter future. The location is ideal for an unforgettable trip, and we are excited to put together a truly outstanding technical, yet also fun, program.

On behalf of the Organizing Committee,

Professor Elefteria (Elia) Psillakis
Chair EuSP2024 | GSAC2024

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1. General Information

Conference topics

EuSP2024 |GSAC2024 cover a wide range of topics that relate to recent advances in research and practice. Green Sample Preparation will be a common topic for discussion at EuSP2024 and GSAC2024

For the 3rd **European Sample Preparation Conference (EuSP2024)**, we solicited original contributions in the following topic areas:

- Fundamentals of sample preparation
- New extraction solvents and materials with improved and tailored properties
- New extraction technologies
- Green sample preparation
- Bioanalysis and in-vivo analysis
- Commercial developments and markets
- Microfluidics/Lab-on-a-chip
- New strategies in omics
- Sample preparation for on-site analysis
- Environmental analysis
- Food control and analysis
- Natural products, fragrance analysis
- Forensic analysis
- Biopharmaceuticals
- Industrial applications

For the **2nd Green and Sustainable Analytical Chemistry Conference (GSAC2024)**, we solicited original contributions in the following topic areas:

- New solvents, materials and modifiers enabling improved and greener processes
- Green chromatography and related techniques
- New technologies to replace existing hazardous ones
- Sensors, on-site and real time analysis
- Direct analytical techniques
- Greenness evaluation
- Miniaturization
- New technologies and techniques that optimize resource efficiency, reduce energy demand and waste generation
- Open-source software and hardware for analysis
- Green sample preparation
- Green Analytical Chemistry applications
- Commercial breakthrough developments
- Green and Sustainable Analytical Chemistry in Education

Venue

The conferences' venue is the Center of Mediterranean Architecture and the Mikis Theodorakis Theater Hall, two adjacent, iconic and historical monuments, located in the heart of the old harbor of Chania.
The Center of Mediterranean Architecture, also known as "Grand Arsenal" (Great Arsenal), is the last of a series of 17 arsenals located in the old harbor of Chania. Its construction started in 1585, followed by the addition of the second floor, in 1872. It had been used as the school of the Christian community in the late 19th century and hosted numerous theater performances (1892), the public hospital (1923) and the Chania

Town Hall (1928 – 1941). In 2002, it has been transformed into an impressive venue for events, conferences and exhibitions. Undoubtably, the contemporary architectural features of this building will provide an inspiring backdrop to the conference.

The stone building Mikis Theodorakis Theater Hall, named after the great Cretan composer Mikis Theodorakis, was built in 1912 during the presidency of El. Venizelos, and originally housed the Customs House in the Venetian harbour of Chania. For that reason, the building was widely known as the "Old Customs House". Recently, it has been renovated and is currently operating as a cultural and convention center.

About Chania and Crete

The island of Crete (also seen as Kreta or Kriti) is the most versatile and exciting destination in Greece. The natural beauty and exquisite archaeological sites, the genuine hospitality, the pristine beach with crystal clear waters and the scrumptious and healthy cuisine offers visitors unique experiences.

The city of Chania is the capital of the Prefecture of Chania. Archeological findings state that the city was built over the ruins of the ancient city of Kydonia and indeed Chania is a place where different civilizations have flourished throughout the centuries. The old town was built around the Venetian port and evidence can be seen from each of these civilizations. It's maze-like alleys with its beautiful Venetian mansions, fountains and elaborate churches offer visitors a plethora of routes to discover.

Plenary Lectures

Four plenary lectures are scheduled during EuSP2024|GSAC2024 (listed in order of appearance):

- **D. Barceló** from the University of Almeria, Spain will present a lecture entitled: "Microplastics in the Environment: Analytical Chemistry Methods, Sorption Material, Risks and Sustainable Solutions".
- **L. Ramos** from the Spanish Scientific Research Council, Spain will present a lecture entitled: "Deep Eutectic Solvents: A Green Approach to the Analysis of Organic Pollutants in Complex Foodstuffs".
- **Cifuentes** from CIAL, National Research Council of Spain, Spain will present a lecture entitled: "Progresses in the Foodomics Study of Natural Green Extracts against Alzheimer's Disease".
- **S. Pedersen-Bjergaard** from the University of Oslo, Norway will present a lecture entitled: "Electromembrane Extraction – Quo vadis".

Keynote lectures

The following keynote lectures listed in order of appearance are scheduled during EuSP2024|GSAC2024:

- "Leveraging Plastic's Potential in Sample Preparation" by **J.M. Herrero-Martínez,** University of Valencia, Spain.
- "Nanofibers: Advanced Format of Organic Polymer-Based Materials for Sample Preparation in HPLC"by F**. Švec**, Lawrence Berkeley National Laboratory, USA
- "Advanced Extraction Techniques Followed by GC-MS/MS and LC-MS/MS for the Determination of Hazardous Chemicals from Tire Microplastics" by M. Llompart**,** University of Santiago de Compostela, Spain
- "An Overview of Molecularly Imprinted Polymers for the Green Analysis of Pharmaceuticals by Electrochemical Sensing" by **S.A. Ozkan**, Ankara University, Turkey
- "Deep Eutectic Solvents in Microextraction: Benefits and Limitations" by **L. Vidal**, University of Alicante, Spain
- "Assessment of Analytical Systems by Metric Tools" by **F. Pena-Pereira**, University of Vigo, Spain
- "Research Progress in Solid-Phase Microextraction" by **G. Ouyang**, Sun Yat-sen University, China
- **"**SPME for Trace Metal Speciation" by Z. Mester, National Research Council of Canada, Canada

- “What 3D Printing Has to Offer in the Liquid Phase Microextraction Field” by **M. Miró**, University of the Balearic Islands, Spain
- “Extraction Strategies for Studies of Plant-Insect and Environmental Contaminant Interactions” by **E. Stashenko,** Universidad Industrial de Santander Bucaramanga, Colombia
- “Combining Microextraction and Mass Spectrometry Using (Bio)Polymer Sorptive Phases Hosted in Stainless Steel Needles” by **R. Lucena**, University of Córdoba, Spain
- “New Bio-Based and Green Solvents at High Pressure: An Option to Improve the Sustainability of Sample Preparation Methods by **E. Ibáñez**, CIAL, Spain
- “Advances in Sample Preparation for the Analysis of Aromatic Amines as Biomarkers in Urine” by **T.C. Schmidt**, University of Duisburg-Essen, Germany
- “Miniaturizing the Already Miniaturized: New Ways to Achieve Dispersion of Magnetic Sorbents in the Analysis of Low-Volume Samples” by **A. Chisver**t, University of Valencia, Spain
- “Improved Analysis of Complex Samples Thanks to More Environmentally-Friendly and Selective Sample Preparation Methods” by **V. Pichon**, Sorbonne University, France
- “Green, Sustainable and Circular Separation Science” by **B. Chankvetadze**, Tbilisi State University, Georgia

Invited lectures

The following invited lectures listed in order of appearance are scheduled during EuSP2024|GSAC2024:

- “Low Solvent Consumption Online Liquid-Gas Chromatography-Tandem Mass Spectrometry for Polycyclic Aromatic Hydrocarbon Determination in Olive Oil” **M. Zoccali**, University of Messina, Italy
- “The Complex World of Eutectic Solvents and Their Use in Sample Preparation” by **A. Gentili**, Sapienza University, Italy
- “Blueness: Criterion in Chemical Analysis” by **V. Samanidou**, Aristotle University of Thessaloniki, Greece
- “Potential of Deep Eutectic Solvents in the Extraction of Pesticides from Plant Foods by **C. Fanali**, Università Campus Bio-Medico di Roma, Italy
- “From “Green” to “Sustainable” Sample Preparation in the Analysis of Natural Products: Opportunities from New Materials Combined with Microextraction Techniques by **C. Cagliero**, University of Turin, Italy
- “Sample Preparation and GC×GC: Fundamental Alleys to Unravel MOSH and MOAH Contamination” by G**. Purcaro**, University of Liege, Belgium
- “Unconventional Solvents in Sample Preparation – Challenges Between Green and White Analytical Chemistry” by **S. Ražić**, University of Belgrade, Serbia
- “New Developments in Bioanalytical Applications of Solid Phase Microextraction” by **E. Boyaci**, Middle East Technical University, Turkey.

Special Issue in "Advances in Sample Preparation"

To celebrate the 3rd European Sample Preparation Conference (EuSP2024) and the 2nd Green and Sustainable Analytical Chemistry Conference (GSAC2024), we have created a Special Issue “**EuSP2024|GSAC2024: Advances in sample preparation and green analytical chemistry**” that will collect high-quality manuscripts presented at the joint conferences. The Special Issue will appear in the Elsevier journal Advances in Sample Preparation, directly associated with our EuChemS-DAC Sample Preparation Study Group and Network. **Advances in Sample Preparation was recently awarded an Impact Factor of 5.2 (IF=5.2)** from Clarivate Analytics in the 2024 Journal Citation Reports (JCR 2024) and was ranked as a **Q1 Journal**.
The Special Issue is open for submissions and the **manuscript submission deadline** is **1st December 2024** with the tentative publication date of the special issue in March 2024. **A full fee waiver is granted for our participants** and the open access feature of our journal will make this special issue freely available to

the public, accessible to readers without subscriptions. The accepted papers will be published online as soon as they have successfully passed the peer-review process.

Submissions to the Special Issue must be done through the Elsevier Editorial Manager online reviewing system on: https://www.editorialmanager.com/sampre/default.aspx

More information on the guidelines for preparing manuscripts and the submission process can be found at: https://www.sciencedirect.com/journal/advances-in-sample-preparation/publish/guide-for-authors

Awards

EuSP2024|GSAC2024 Young Innovator Award

The key theme of the EuSP2024|GSAC2024 joint events is "Innovation", aligning with the 2024 annual theme of EuChemS-DAC Sample Preparation Study Group and Network. To celebrate this theme, the "EuSP2024|GSAC2024 Young Innovator Award" is being launched. This award will honor early-career researchers who demonstrate exceptional technical advancement and innovation in the field of sample preparation or green analytical chemistry.

The award is open worldwide to researchers who are at an early stage of their career, either pursuing a PhD or having completed their PhD within the last ten years. The winner will be selected by a committee comprising members from both industry and academia. Applicants can expect to receive social media attention and international recognition for their innovation. The winner of the award will be announced during the closing ceremony and will receive an award plaque and an honorarium of 300 Euro.

Prize for the best student oral presentation from the RSC Separation Science group

The Royal Society of Chemistry Separation Science group would be pleased to award a prize for the best student oral presentation. This will be in the form of a grant of £500 towards attendance at the SinS conference in Brighton UK, from 15th to 17th July 2025.

Solutions in Science (SinS) is a conference and exhibition organised by International Labmate the publishers of International Labmate, Labmate UK and Chromatography Today in partnership with the Royal Society of Chemistry (The RSC), BMSS, ChromSoc and like-minded associations. "SinS" brings together scientists and analytical chemists to discuss and explore the latest products, techniques and analytical Solutions.

Best oral presentation prize for a young researcher

The EuChemS-DAC Sample Preparation Study Group and Network will sponsor one prize for the best student oral presentation given by a young researcher, valued at 250 €.

Best poster prizes sponsored by Chemistry Europe

Chemistry Europe sponsors three best poster prizes in the form of book vouchers, valued at **150 €** each.

The Chemistry Europe sponsorship program is a contractual arrangement between the Chemistry Europe Partner Societies.

Courses/Workshops

Pre-conference Course: Greenness evaluation of sample preparation methods by AGREEprep (IUPAC project 2021-015-2-500)

Free short course sponsored by the IUPAC project 2021-015-2-500, open to all registered participants of EuSP2024|GSAC2024. The course will explore the use of the AGREEprep metric tool for evaluating the greenness of sample preparation methods. There are no fees to attend this course. A limited number of places are available and will be allocated on a "first-come, first-served" basis.

Instructors: F. Pena-Pereira, J.L. Benedé

Content:

1. Elucidation of the concept of Green Sample Preparation

2. Requirements of metric tools for the assessment of the green profile of sample preparation methods: Introduction of AGREEprep
3. An overview of the IUPAC Project on the Greenness of official standard sample preparation methods
4. Exemplification of AGREEprep metric tool to assess the greenness of official standard sample preparation methods
5. Practical work and Q&A

Expected outcomes:

By the end of this workshop, participants are expected to:

1. Acquire relevant knowledge on the principles of Green Sample Preparation;
2. Learn the metric tools available for evaluating the greenness of sample preparation methods and elucidate their differences;
3. Identify the ideal requirements that these metric tools should present depending on the method to be evaluated;
4. Accurately apply one of these tools (*i.e.,* AGREEprep) in the assessment of the greenness of sample preparation methods by selecting the appropriate items and values

Workshop: Supporting young researchers in their publishing careers: Author and reviewer workshop

Free workshop sponsored by Elsevier, open to all registered participants of EuSP2024|GSAC2024. In order to support young researchers and make the road to publication a bit smoother, this workshop offers advice and information on how to write a manuscript, the submission procedures, publication ethics, peer review and many other topics. The workshop is open to all registered participants of EuSP2024|GSAC2024.

Instructors: Rob van Daalen (Journal Publisher, Elsevier) and Damia Barcelo (Editor, Elsevier)

Workshop: AI Tools for Publishing and Research

Free workshop sponsored by Chemistry Europe, open to all registered participants of EuSP2024|GSAC2024. Artificial Intelligence (AI) Tools are becoming more popular and increasingly easy to use today. This talk provides editorial insights on the most common tools that scientists might find helpful in preparing their manuscripts and organizing their research output. We'll also cover the basic issues on limitations, ownership, confidentiality, accuracy, and disclosure when it comes to such AI tools. At the end, attendees will be able to understand the pros and cons of such tools and best practices in using them.

Instructor: David Peralta, Editor, Wiley-VCH

SRA Instruments Seminar: Green Approach to Intensive Automation of Olive Oil Analysis According to EU Regulation

Description: The COMMISSION REGULATION (EEC) No 2022/2104 currently in force throughout the European community, defines the characteristics necessary to ascribe the various olive oils to the different product classes (lampante, virgin, extra virgin, refined, composed, crude/refined/olive pomace). In order to commercialize the various oils within the correct class of belonging, community producers and distributors must produce analytical evidence regarding the determination of numerous chemical, chemical-physical and organoleptic-sensorial parameters. In many cases, the analytical methods are highly time-consuming, require the use of high amounts of organic solvents and consumables materials, and constitute a potential source of continuous and prolonged exposure of operators to chemical vapors.

SRA instruments Italy has developed a series of automated analyzers able to drastically reduce the use of solvents (up to 90% solvent amount saved), and consumables materials (up to 95% amount saved), as well as the exposure of the analysts to organic solvents (practically eliminated), fully automating the whole analysis workflows, and therefore assuring the highest level of data reliability. The analyzers are suitable for the determination of Alkyl esters, Waxes, Stigmastadienes, Sterols, Triterpene dialcohols; in all cases, the only operation to be carried out manually is the initial weighing of an aliquot of sample to be placed on the tray.

Speaker: Andrea Carretta, SRA Instruments

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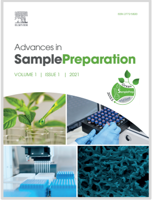
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EuChemS, the European Chemical Society, aims to nurture a platform for scientific discussion and to provide a single, unbiased European voice on key policy issues in chemistry and related fields.

Representing more than 160,000 chemists from more than 40 Member Societies and other chemistry related organisations, EuChemS relies on a unique network of active researchers involved in all the fields of chemistry. Through this network, EuChemS organises several specialised academic conferences as well as the biannual EuChemS Chemistry Congress, the European congress of chemical sciences. EuChemS also promotes the role and image of the chemical sciences among the general public and policy-makers through social media, newsletters and through the organisation of conferences and workshops open to the society.

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For more information about the European Chemical Society (EuChemS), please visit www.euchems.eu or contact us at:

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Advances in Sample Preparation

1st Impact Factor 5.2!

Advances in Sample Preparation received its first Impact Factor in June this year. An IF 5.2 is amazing and shows the importance of the journal and interest in the field. SAMPRE publishes articles on all aspects of sample preparation. The journal welcomes submissions on fundamental and applied topics, covering discoveries in fundamentals, innovations in new extraction principles, materials, techniques and technologies, miniaturization, in vivo and on site sampling, automation, hyphenation and green sample preparation

Meet the Editors

Elefteria Psillakis (Editor-in-Chief)

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Rafael Lucena

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Lourdes Ramos

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3. Scientific Programme at a Glance

**Sunday
15th September**

13:00	Registration (CMA)	
14:00	Registration	Short Course (Mikis T.)
17:00	Registration (CMA)	
18:00	Opening Ceremony (Mikis T.)	
18:30	Opening Plenary Lecture (Mikis T.)	
19:10	Welcome Reception (CMA)	

**Monday
16th September**

	Mikis T. Hall	CMA Hall
08:00	Registration	
09:00	Plenary Lecture Mikis T. Hall	
09:40		
09:45	Keynote Session 1	Keynote Session 2
10:05	Oral Session 1	Oral Session 2
10:50	Coffee Break/ Poster Session A/ Exhibition (Mikis T.)	
11:30	Keynote Session 3	Keynote Session 4
11:50	Oral Session 3	Oral Session 4
12:50	Lunch Break (CMA)	
13:50	Workshop (Mikis T.)	
14:20	Coffee Break/ Poster Session B/ Exhibition (Mikis T.)	
15:00	Keynote Session 5	Keynote Session 6
15:20	Oral Session 5	Oral Session 6
16:05	Coffee Break/ Exhibition (Mikis T.)	
16:30	Keynote Session 7	Keynote Session 8
16:50	Oral Session 7	Oral Session 8
17:50		

**Tuesday
17th September**

	Mikis T. Hall	CMA Hall
08:00	Registration	
09:00	Plenary Lecture Mikis T. Hall	
09:40		
09:45	Keynote Session 9	Keynote Session 10
10:05	Oral Session 9	Oral Session 10
10:50	Coffee Break/ Poster Session C/ Exhibition (Mikis T.)	
11:30	Keynote Session 11	Keynote Session 12
11:50	Oral Session 11	Oral Session 12
12:50	Lunch Break (CMA)	
13:50	Vendor Seminar (Mikis T.)	
14:20	Coffee Break/ Poster Session D/ Exhibition (Mikis T.)	
15:00	Young Researchers Session 1	Young Researchers Session 2
15:50	Coffee Break/ Exhibition (Mikis T.)	
16:20	Workshop (Mikis T.)	Round Table Discussion (CMA)
17:00	Young Researchers Session 3	Young Researchers Session 4
17:50		
19:30	Bus Transfer	
20:00	Cofenrence Dinner (ticket required)	

**Wednesday
18th September**

	Mikis T. Hall
09:00	Keynote Session 13 Oral Session 13 Keynote Session 13
10:25	Coffee Break Exhibition
11:00	Keynote Session 14 Oral Session 14 Keynote Session 14
12:25	Lunch Break (CMA)
14:00	Closing Plenary Lecture
14:40	Closing Ceremony/ Awards/ Presentation EuSP2026|GSAC2026
15:30	Farewell Coffee
17:00	Guided tour to the old harbour of Chania
18:30	

**Mikis Theodorakis (Mikis T.): Lectures, Coffee Breaks, Poster Sessions, Exhibition
Center of Mediterannean Architecture (CMA): Lectures, Lunches, Welcome Reception**

4. Scientific Programme – Detailed Schedule

Sunday, 15th September

13:00 - 18:00 **Center of Mediterranean Architecture**

Registration

14:00 - 17:00 **Mikis Theodorakis Hall**

Short Course: Greenness evaluation of sample preparation methods by AGREEprep (IUPAC project 2021-015-2-500)

Instructors: F. Pena-Pereira, J.L. Benedé

18:00 - 19:10 **Mikis Theodorakis Hall**

Opening Session

Chairs: E. Psillakis, S. Ražić

18:00 - 18:30	**Opening Ceremony**
18:30 - 19:10	**PL-01 Microplastics in the Environment: Analytical Chemistry Methods, Sorption Material, Risks and Sustainable Solutions** D. Barceló

19:10 **Center of Mediterranean Architecture**

Welcome Reception

Monday, 16th September

9:00 - 9:40 **Mikis Theodorakis Hall**

Plenary Lecture

Chairs: A. Chisvert, L. Vidal

09:00 - 09:40 **PL-02 Deep Eutectic Solvents: A Green Approach to the Analysis of Organic Pollutants in Complex Foodstuffs**
L. Ramos

9:45 - 10:50 **Mikis Theodorakis Hall**

Oral Session: New Materials and Devices

Chairs: A. Chisvert, L. Vidal

09:45 - 10:05 **KN-1 Leveraging Plastic's Potential in Sample Preparation**
J.M. Herrero-Martínez, M.J. Lerma-García, M. Beneito-Cambra, E.J. Carrasco-Correa, M. Verga-Barberán, E.F. Simó-Alfonso

10:05 - 10:20 **O-1 Advanced Sample Preparation Using 3D Printing: From Conventional to Biomimetic Solid-Phase Extraction**
E.J. Carrasco-Correa, M. Vergara-Barberán, M. Beneito-Cambra, M.J. Lerma-García, E.F. Simó-Alfonso, J.M. Herrero-Martínez, M. Miró

10:20 - 10:35 **O-2 Extraction of Emerging Contaminants from Treated Wastewater by a Polymeric Biodegradable Film and Following Analysis by Target and Non-Target LC-MS**
B. Benedetti, E. Ceccardi, H. MacKeown, M. Di Carro, R. Tauler, E. Magi

10:35 - 10:50 **O-3 Functionalized Membranes for Unveiling Metal Interactions with Microplastics and Organic Pollutants in Aquatic Systems**
C. Fontàs, N. Khatir, E. Anticó

9:45 - 10:50 **Center of Mediterranean Architecture Hall**

Oral Session: Green Analysis

Chairs: E. Ibañez, V. Samanidou

09:45 - 10:05 **KN-2 Nanofibers: Advanced Format of Organic Polymer-Based Materials for Sample Preparation in HPLC**
F. Švec, P. Chocholouš, L. Chocholoušová Havlíková, J. Chvojka, J. Erben, A. Háková, H. Kholová, I. Lhotská, M. Raabová, D. Šatínský

10:05 - 10:20 **INV-1 Low Solvent Consumption Online Liquid-Gas Chromatography-Tandem Mass Spectrometry for Polycyclic Aromatic Hydrocarbon Determination in Olive Oil**
M. Zoccali, A. Arena, P.Q. Tranchida, L. Mondello

10:20 - 10:35 **O-4 Here, There and Everywhere - Sustainable Solutions for Liquid Chromatography**
S. Lamotte, M. Legelli, M. Wirtz

10:35 - 10:50 **O-5 Automated Preparation and Analysis of Dried Blood Spot Samples Collected by Volumetric Microsampling**
P. Kubáň, M. Dvořák, R. Maršala

10:50 - 11:30 **Mikis Theodorakis Exhibition Area**

Poster Session A

Sponsors Exhibition

Coffee Break

11:30 - 12:50 **Mikis Theodorakis Hall**

Oral Session: Environmental Analysis

Chairs: Z. Mester, G. Ouyang

11:30 - 11:50 **KN-3 Advanced Extraction Techniques Followed by GC-MS/MS and LC-MS/MS for the Determination of Hazardous Chemicals from Tire Microplastics**
M. Llompart, A. Duque-Villaverde, S. Sóñora, V. Carballeira, D. Armada, T. Dagnac

11:50 - 12:05 **O-6 Analysis of Volatile Methylsiloxanes in Several Environmental Matrices at LEPABE**
N. Ratola, V. Homem, A. Alves

12:05 - 12:20 **O-7 Analysis of PFAAs and Fluorotelomer Alcohols in Shower Curtains: Focus on Migration Conditions**
F. Lucarini

12:20 - 12:35 **O-8 SMART: Sustainable Membranes as Affordable and Reliable Tools for Environmental Monitoring of Pharmaceuticals**
F. Merlo, R. Ghiglione, C. Fontàs, A. Cabrera-Codony, A. Speltini, E. Anticò, A. Profumo

12:35 - 12:50 **O-9 On-Site Quantitation of BTEX in Atmospheric Air Using Solid-Phase Microextraction and Gas Chromatography with Photoionization Detector**
B. Kenessov, T. Kurmanbayeva, B. Bukenov, Z. Rymzhanova, N. Kazhkenova, A. Imangabassov, A. Smail, N. Karimkyzy

11:30 - 12:50 **Center of Mediterranean Architecture Hall**

Oral Session: Green Sensors

Chairs: S. Pedersen-Bjergaard, V. Pichon

11:30 - 11:50 **KN-4 An Overview of Molecularly Imprinted Polymers for the Green Analysis of Pharmaceuticals by Electrochemical Sensing**
S.A. Ozkan

11:50 - 12:05 **O-10 Paper-Based Electroanalytical Devices Equipped with CO_2 Laser-Assembled Nanostructured Conductive Films**
F. Della Pelle, A. Scroccarello, F. Silveri, D. Paolini, S. Fiori, D. Compagnone

12:05 - 12:20 **O-11 Immobilization of Metal-Organic Frameworks in 3D Printed Devices for the Development of Fluorescent and Colorimetric Sensors Used in the Detection of Antibiotics and Heavy Metals**
M.A. Vargas-Muñoz, L. Maza, L. Ferrer, E. Palacio

12:20 - 12:35 **O-12 Greening Electrochemical (EC) Analysis & Biosensing: From EC Mini-cell to Sustainable EC Sensor Solutions**
A. Schulte

12:50 - 14:20 **Center of Mediterranean Architecture**

Lunch Break

13:50 - 14:20 **Mikis Theodorakis Hall**

Workshop: AI Tools for Publishing and Research

Instructor: D. Peralta, Editor, Wiley-VCH

14:20 - 15:00 **Mikis Theodorakis Exhibition Area**

Poster Session B

Sponsors Exhibition

15:00 - 16:05 **Mikis Theodorakis Hall**

Oral Session: Deep Eutectic Solvents

Chairs: S. Cárdenas, L. Ramos

15:00 - 15:20 **KN-5 Deep Eutectic Solvents in Microextraction: Benefits and Limitations**
L. Vidal, S. Abellán, I. Rubio, C. Zapater, M.A. Aguirre, A. Canals

15:20 - 15:35 **INV-2 The Complex World of Eutectic Solvents and Their Use in Sample Preparation**
A. Gentili, C. Dal Bosco, A. Martinelli, P. D'Angelo, S. Fanali, C. Fanali

15:35 - 15:50 **O-14 Natural Deep Eutectic Solvent-Based Liquid Phase Microextraction in a 3D-Printed Microfluidic Flow Cell for the On-Line Determination of Thiabendazole**
M. Díaz-Álvarez, E. Turiel, A. Martín-Esteban

15:50 - 16:05 **O-15 Evaluation of Deep Eutectic Solvents in the Synthesis of Molecularly Imprinted Fibers for the Solid-Phase Microextraction of Triazines in Soil**
A. Martín-Esteban, A. Monnier, E. Turiel, M. Díaz-Álvarez

15:00 - 16:05 **Center of Mediterranean Architecture Hall**

Oral Session: Green Metrics

Chairs: J. L. Benedé, E. Psillakis

15:00 - 15:20 **KN-6 Assessment of Analytical Systems by Metric Tools**
F. Pena-Pereira

15:20 - 15:35 **INV-3 Blueness: Criterion in Chemical Analysis**
V. Samanidou

15:35 - 15:50 **O-16 Greenness of Sample Preparation for Proteomic Analysis**
K. Maráková, M. Opetová, R. Tomašovský, K.A. Schug

15:50 - 16:05 **O-17 Multi-Criteria Decision Analysis for Selection of Greener Chemicals for Analytical Chemistry**
M. Tobiszewski

16:05 - 16:30 **Mikis Theodorakis Exhibition Area**
Coffee Break
Sponsors Exhibition

16:30 - 17:50 **Mikis Theodorakis Hall**
Oral Session: Microextraction
Chairs: M. Llompart, A. Martín-Esteban

16:30 - 16:50 **KN-7 Research Progress in Solid-Phase Microextraction**
G. Ouyang

16:50 - 17:05 **O-18 Green Microextraction Techniques for DBPs Monitoring**
A. Agapiou, P. Papaioakeim, E.A. Elia

17:05 - 17:20 **O-19 Assessing Water Quality: Fast, High Sensitivity Analysis of Chlorophenols and Other Common Odorants by Automated HiSorb**
L. Hearn, R. Cole, R. Szafnauer, M. Santoro

17:20 - 17:35 **O-20 SBSE to Overcome Analytical Challenges for Next-Generation Product Registration**
B. Gruber, E. Eberspach, S. Luederwald

17:35 - 17:50 **O-21 Use of the Cold Block Digestion Technique for Multi-Element Analysis of Geological Samples**
L. Marjanovic

16:30 - 18:05 **Center of Mediterranean Architecture Hall**
Oral Session: Environmental Monitoring
Chairs: A. Gentili, N. Ratola

16:30 - 16:50 **KN-8 SPME for Trace Metal Speciation**
Z. Mester

16:50 - 17:05 **O-22 New Sample Preparation Strategies for the Control of VOC in Wood-Based Panels**
R.M. Ramos, F.D. Gonçalves, R.T. Fernandes, J.R. Santos, J.A. Rodrigues

17:05 - 17:20 **O-23 Biomass Cooking and Air Quality: A Study on Volatile Organic Compounds via Thermal Desorption GC-MS**
I. Kozyatnyk, A. Rebryk, M. Njenga

17:20 - 17:35 **O-24 On the Determination of the Photodegradation Extent of Microplastics: Lights and Shadows of Micro-FTIR Spectroscopy**
E. Conterosito, M. Roncoli, C. Ivaldi, E. Perin, B. De Felice, S. Gazzotti, M.A. Ortenzi, M. Parolini, V. Gianotti

17:35 - 17:50 **O-25 X-ray Fluorescence-Based Studies of Particulate Matter on Filter**
D. Eichert, T. Hase, L. Borgese

Tuesday, 17th September

9:00 - 9:40 **Mikis Theodorakis Hall**

Plenary Lecture

Chairs: G. Purcaro, E. Stashenko

09:00 - 09:40 **PL-03 Progresses in the Foodomics Study of Natural Green Extracts against Alzheimer's Disease**
A. Cifuentes, G. Alvarez, J.A. Mendiola, E. Ibáñez, A. Valdés

9:45 - 10:50 **Mikis Theodorakis Hall**

Oral Session: Miniaturization

Chairs: E.J. Carrasco-Correa, J. M. Herrero-Martínez

09:45 - 10:05 **KN-9 What 3D Printing Has to Offer in the Liquid Phase Microextraction Field**
M. Miró, A. Sahragard, P. Kubáň, E.J. Carrasco-Correa

10:05 - 10:20 **O-26 3D-Printed Millifluidic Extraction Devices Encompassing Solid and Liquid Biopolymeric Phases**
F.A. Casado-Carmona, R. Lucena, S. Cárdenas, M. Miró

10:20 - 10:35 **O-27 Metal Nanoparticles Laser Writing on Cellulosic Substrates for Affordable Colorimetric Paper-Based Analytical Device Development**
A. Scroccarello, F. Della Pelle, P. Di Battista, D. Compagnone

10:35 - 10:50 **O-28 A Composite Hydrogel Beads for Vortex-Assisted Dispersive Micro-Solid Phase Extraction of Food Additives Followed by HPLC-DAD**
P. Nurerk, O. Bunkoed, M. Llompart, S. Hongyok

9:45 - 10:50 **Center of Mediterranean Architecture Hall**

Oral Session: Natural Product Analysis

Chairs: A. Gentili, L. Ramos

09:45 - 10:05 **KN-10 Extraction Strategies for Studies of Plant-Insect and Environmental Contaminant Interactions**
E. Stashenko

10:05 - 10:20 **INV-4 Potential of Deep Eutectic Solvents in the Extraction of Pesticides from Plant Foods**
C. Fanali**,** S. Della Posta, M. Gherardi, A. Gentili, L. De Gara

10:20 - 10:35 **INV-5 From "Green" to "Sustainable" Sample Preparation in the Analysis of Natural Products: Opportunities from New Materials Combined with Microextraction Techniques**
C. Cagliero, G. Bechis, A. Marengo, B. Sgorbini, P. Rubiolo

10:35 - 10:50 **O-29 Effects of Different Extraction Methods on Antioxidant Properties of Seaweeds**
V. F. Domingues, F. Santos, S. Morais, M.J. Ramalhosa, C. Soares, C. Delerue-Matos

10:50 - 11:30 Mikis Theodorakis Exhibition Area

Poster Session C

Sponsors Exhibition

Coffee Break

11:30 - 12:50 Mikis Theodorakis Hall

Oral Session: Green Separations & Couplings

Chairs: T. Schmidt, M. Zoccali

11:30 - 11:50 **KN-11 Combining Microextraction and Mass Spectrometry Using (Bio)Polymer Sorptive Phases Hosted in Stainless Steel Needles**
R. Lucena, J. Millán-Santiago, S. Cárdenas

11:50 - 12:05 **INV-6 Sample Preparation and GC×GC: Fundamental Alleys to Unravel MOSH and MOAH Contamination**
G. Purcaro, A. Gorska, G. Bauwens

12:05 - 12:20 **O-30 Dynamic Headspace Vacuum In-Tube Extraction and GC-MS for Analyzing Volatile Compounds in Various Matrices**
L.K. Tintrop, P. Fuchsmann

12:20 - 12:35 **O-31 Breaking Barriers with Automation: Automated Vac-HS-SPME for Enhanced Detection and Workflow Efficiency**
C. Liscio, K. Ridgway

12:35 - 12:50 **O-32 Microextraction Strategies for Lipid Peroxidation Analysis in Infant Formulae**
J.A. Custodio-Mendoza, M.A. Kurek, A.M. Carro

11:30 - 12:50 Center of Mediterranean Architecture Hall

Oral Session: Green Solvents

Chairs: C. Fanali, J.L. Benedé

11:30 - 11:50 **KN-12 New Bio-Based and Green Solvents at High Pressure: An Option to Improve the Sustainability of Sample Preparation Methods**
E. Ibáñez, M. Strieder Martins, C.A. Balbinot, J.A. Mendiola, M.A. Rostagno, A. Cifuentes, M. Lanza, S.R.S. Ferreira

11:50 - 12:05 **INV-7 Unconventional Solvents in Sample Preparation – Challenges Between Green and White Analytical Chemistry**
S. Ražić

12:05 - 12:20 **O-33 Investigation of Greener Solvents for HPLC**
F. Michel, B. Peters, G. Jung, A. Piper, P. Knoell, P. Lewits, E. Machtejewas

12:20 - 12:35 **O-34 Structural Characterization of Hydrophilic Natural Deep Eutectic Solvents, Evaluation of its Physicochemical Properties and Application to Extract Phenolic Compounds from Tea Samples**
L. Carbonell-Rozas, R. Romero-González, A. Garrido Frenich

12:35 - 12:50 **O-35 Miniaturized Stir Bar Dispersive Liquid Microextraction (mSBDLME) along with Natural Deep Eutectic Solvent-Based Ferrofluids: A Perfect Match**
J. Grau, J.L. Benedé, A. Chisvert

12:50 - 14:20 **Center of Mediterranean Architecture**

Lunch Break

13:50 - 14:20 **Mikis Theodorakis Hall**

Vendor Seminar: Green Approach to Intensive Automation of Olive Oil Analysis According to EU Regulation

Speaker: Andrea Carretta, SRA Instruments

14:20 - 15:00 **Mikis Theodorakis Exhibition Area**

Poster Session D

Sponsors Exhibition

15:00 - 15:50 **Mikis Theodorakis Hall**

Oral Session Young Researchers I

Chairs: M. Miró, L. Vidal

15:00 - 15:10 **YO-1 In Vitro Bioaccessibility Assessment of Tire Related Compounds, Including 6PPD and 6PPDq, Using Simulated Fluids**
S. Sóñora, A. Duque-Villaverde, D. Armada, T. Dagnac, M. Llompart

15:10 - 15:20 **YO-2 Vacuum-Assisted Headspace Solid-Phase Microextraction of Tomato Volatiles During Ripening**
A. Pateraki, E. Psillakis

15:20 - 15:30 **YO-3 Advancements in LC-MS/MS Methodology: Quantification of Six Phosphatidylethanol Homologues in Whole Blood with Minimized Phospholipid Interference**
M.H. Maria, N.R. Neng, T. Berg

15:30 - 15:40 **YO-4 Coupling Miniaturized Stir Bar Sorptive Dispersive Microextraction to Needle-Based Electrospray Ionization Emitters for Mass Spectrometry**
A.L. López-Juan, J. Millán-Santiago, J.L. Benedé, A. Chisvert, R. Lucen, S. Cárdenas

15:40 - 15:50 **YO-5 Gas-Diffusion Microextraction as a Sustainable Sample Preparation to Determine Fragrance Allergens**
A. Castiñeira-Landeira, A. Gomez-Feas, A.M. Carro, T. Dagnac, I.M. Valente, J.A. Rodrigues, P.J. Almeida, M. Llompart

15:00 - 15:50 **Center of Mediterranean Architecture Hall**

Oral Session Young Researchers II

Chairs: C. Cagliero, S. Ražić

15:00 - 15:10 **YO-6 Biomimetic Tools for Selective Solid-Phase Extraction of Pesticides in Water Intended for Human Consumptions**
N. Khaldi, A. Combès, M. Legal, V. Pichon, N. Delaunay

15:10 - 15:20 **YO-7 Advancement of Resistive Pulse Sensing for Particle Identification and Use on Environmental Samples**
E. Christie, M. Platt

15:20 - 15:30 **YO-8 Spot Test Method for Tetracycline Using Molecularly Imprinted Polymer-Coated Paper Integrated into a Portable 3D-Printed Platform with Smartphone-Based Fluorescent Detection**
D. Barzallo, E. Palacio, L. Ferrer, M. del Pilar Taboada Sotomayor

15:30 - 15:40 **YO-9 High-Throughput Spectrofluorimetric Determination of Acetone in Real Water Samples**
P. Michel, B. Coulomb, F. Robert-Peillard, J.L. Boudenne

15:40 - 15:50 **YO-10 Cellulose Acetate Microbeads Recovered from Cigarette Filters in Packed Bed Column for Water Remediation Applications**
M.G. De Cesaris, L. Antonelli, S. Grasso, A. Gentili

15:50 - 16:20 **Mikis Theodorakis Exhibition Area**

Coffee Break

Sponsors Exhibition

16:20 - 17:00 **Mikis Theodorakis Hall**

Workshop: Supporting young researchers in their publishing careers: Author and reviewer workshop

Instructors: R. van Daalen (Journal Publisher, Elsevier) and D. Barcelo (Editor, Elsevier)

16:20 - 17:00 **Center of Mediterranean Architecture Hall**

Round Table Discussion:

Greenness of official standard sample preparation methods (IUPAC project 2021-015-2-500)

Moderator: S. Ozkan

Speakers: S. Lamotte, Z. Mester, F. Michel, E. Psillakis, M. Santoro, M. Wolff

17:00 - 17:50 **Mikis Theodorakis Hall**

Oral Session Young Researchers III

Chairs: M. Miró, L. Vidal

17:00 - 17:10 **YO-11 Vacuum-Assisted SPME-GC×GC-MS for Accurate 5-HMF Determination and Volatile Profiling of Honey**
D. Eggermont, F. Pardi, G. Purcaro

17:10 - 17:20 **YO-12 Converting a Moka-Pot into a Green Extraction Tool for the Analysis of Performance Enhancing Drugs via HPLC-MS/MS in Dietary Supplements**
M. Baglietto, B. Benedetti, E. Castrignanò, M. Di Carro, K. Wolff, E. Magi

17:20 - 17:30 **YO-13 Advantages of the Use of Microwave-Assisted Technology for Lipid Analysis**
D. Ferrara, M. Beccaria, C.E. Cordero, G. Purcaro

17:30 - 17:40 **YO-14 Development of Novel Volatile Extraction Method for Raw and Cooked Beef Steak Using High Capacity Sorptive Extraction Thermal Desorption Gas Chromatography Mass Spectrometry**
F. Morsli, D.T. Mannion, P.G. Dunne, A.P. Molony, F.J. Monahan, K.N. Kilcawley

17:40 - 17:50 **YO-15 New Strategies for the Improvement of the Environmental Impact and Overall Performance of the Sample Preparation for Challenging Fragrance Samples**
G. Bechis, A. Marengo, B. Sgorbini, P. Rubiolo, C. Cagliero

17:00 - 17:40 Center of Mediterranean Architecture Hall

Oral Session Young Researchers IV

Chairs: C. Cagliero, S. Ražić

17:00 - 17:10 **YO-16 Synthesis of Sustainable Cyclodextrin-Based Sorbents and Their Application for the Extraction of Organic Contaminants from Environmental Water**
N. Felli, I. Francolini, L.M. Migneco, A. Gentili

17:10 - 17:20 **YO-17 Development of a New Sorbent Material from Rice Husk Ash for the Preconcentration of Perfluoroalkyl Substances in Environmental Waters**
P. Bianchini, F. Merlo, G. Premoli, A. Speltini, A. Profumo

17:20 - 17:30 **YO-18 Per- and Polyfluoroalkyl Substances Losses in Sample Pretreatment: Sample Preparation, Solid Phase Extraction, Filtration, and ENVI-carb Cleaning**
X. Huang, G. Arye, A. Ronen

17:30 - 17:40 **YO-19 Microbeads from Recycled Commercial Polystyrene for the In-Syringe Micro Solid-Phase Extraction of Four Opioids from Environmental and Biological Matrices**
L. Antonelli, A.I. López-Lorente, A. Gentili, R. Lucena, S. Cárdenas

20:00 Nykterida Restaurant

Conference Dinner (Ticket is Required)

Bus Transfer to the Restaurant at 19:30 from the “Clock Tower of Municipal Garden”

Wednesday, 18th September

09:00 - 10:25 **Mikis Theodorakis Hall**

Oral Session: Bioanalysis

Chairs: S. Ozkan, S. Pedersen-Bjergaard

09:00 - 09:20 **KN-13 Advances in Sample Preparation for the Analysis of Aromatic Amines as Biomarkers in Urine**
T.C. Schmidt, N. Lorenzo-Parodi, W. Kaziur-Cegla, A. Gjelstad, E. Leitner

09:20 - 09:35 **INV-08 New Developments in Bioanalytical Applications of Solid Phase Microextraction**
E. Boyaci

09:35 - 09:50 **O-36 Synthesis and Characterization of a Molecularly Imprinted Polymer for Selective Extraction of Chlordecone from Water and Biological Samples**
A. Combès, P. Bosman, M. Lambert, G. Lavison Bompard, V. Pichon

09:50 - 10:05 **O-37 Smart Sampling: “Spot-on” for Advanced Protein Determination from Dried Matrix Spots**
L. Reubsaet, T. Grønhaug Halvorsen

10:05 - 10:25 **KN-14 Miniaturizing the Already Miniaturized: New Ways to Achieve Dispersion of Magnetic Sorbents in the Analysis of Low-Volume Samples**
A. Chisvert, J.L. Benedé, J. Grau, C. Azorín, G. Peris-Pastor, A.L. López-Juan, L.M. Moreno-Calleja

10:25 - 11:00 **Mikis Theodorakis Exhibition Area**

Coffee Break

Sponsors Exhibition

11:00 - 12:25 **Mikis Theodorakis Hall**

Oral Session: Green Sample Preparation and Analysis

Chairs: E. Boyaci, V. Samanidou

11:00 - 11:20 **KN-15 Improved Analysis of Complex Samples Thanks to More Environmentally-Friendly and Selective Sample Preparation Methods**
V. Pichon, A. Combès, N. Delaunay

11:20 - 11:35	**O-38 New Amphoteric Materials for Sorptive Extraction** R.M. Marcé, A. Moral, F. Borrull, P.A.G. Cormack, N. Fontanals
11:35 - 11:50	**O-39 Preconcentration of Bioactive Compounds by New Sorbent Materials: Searching for Sustainability in Solid-Phase Extraction** A. Speltini, F. Merlo, P. Bianchini, G. De Soricellis, E.S. Sammatrice, V. Quarta, L. Ferrari, E. Calleri, C. Milanese, A. Profumo
11:50 - 12:05	**O-40 Planar Sorptive Phases, from Thin Films to Polymeric Coated Particles** S. Cardenas, R. Lucena
12:05 - 12:25	**KN-16 Green, Sustainable and Circular Separation Science** B. Chankvetadze

12:25 - 14:00 **Center of Mediterranean Architecture**

Lunch Break

14:00 - 15:30 **Mikis Theodorakis Hall**

Closing Session

Chairs: M. Llompart, E. Psillakis

14:00 - 14:40	**PL-04 Electromembrane Extraction – Quo vadis** S. Pedersen-Bjergaard
14:40 - 15:30	**Closing Ceremony, Awards, Presentation of EuSP2026|GSAC2026**

15:30 - 17:00 **Mikis Theodorakis Exhibition Area**

Farewell coffee

17:00 - 18:30 **Mikis Theodorakis Exhibition Area**

Guided tour at the old harbour of Chania

Poster Session A

Monday, 16th September | 10:50-11:30

PSA-01 **Biomonitoring of 13 Heavy Metals in Various Types of Leaves from Different Regions of Italy**
T. Pócsová, M. Maio, S. Hrouzková, P. Avino

PSA-02 **Biomimetic Materials and 3D Printing Solid-Phase Microextraction: A Novel Approach to Study Bioaccumulation Factors of Pollutants without the Need of Animal Models**
E.J. Carrasco-Correa, A. Carrió-Roselló, C. Ochoa-Esteso, P. Molina-Brotons, M.J. Lerma-García, M. Miró

PSA-03 **Optimization of a Method Based on MSPD Combined with GC-MS for Determination of Tire Particle Additives in Mussel**
N. Carro, I. García-Alonso, S. Sóñora, A. Duque-Villaverde, I. García, A. Mouteira, M. Ignacio, A.M. Carro, M. Llompart

PSA-04 **Preparation and Evaluation of 3D-Printed Paddle-Stirrer Coated with Polymers of Different Polarity for the Micro-Solid Phase Extraction of Selected Contaminants from Environmental Water Samples**
M. Díaz-Álvarez, A. Monnier, E. Turiel, A. Martín-Esteban

PSA-05 **Paraphenylenediamines and Other Emerging Compounds in Crumb Rubber from Leisure Facilities**
A. Duque-Villaverde, D. Armada, T. Dagnac, M. Llompart

PSA-06 **Analysis of 6PPD, 6PPD-quinone and Other Hazardous Chemicals from Tire Rubber in Natural Waters Using Solid-Phase Microextraction**
A. Duque-Villaverde, V. Carballeira, D. Armada, P. Nurerk, T. Dagnac, M. Llompart

PSA-07 **Pipette-Tip Membrane Microextraction for the Determination of Antibiotics in Natural Waters**
C. Fontàs, L. Portell, B. Alcalde, E. Anticó

PSA-08 **Automated High-Capacity Sorptive Extraction of Volatile Per- and Polyfluoroalkyl Substances (PFAS) from Drinking water**
L. Hearn, R. Szafnauer, H. Calder, M. Santoro

PSA-09 **Dispersive Solid-Phase Extraction Using Alginate/Graphene Oxide Composite Gel Beads for Preconcentration of Heavy Metals in Environmental Water Samples**
K. Kumrić, Đ. Petrović, K. Stanković

PSA-10 **Photodegradation Studies of Tire Rubber Additives in Water Using Solid-Phase Microextraction**
M. Llompart, A. Duque-Villaverde, V. Carballeira, N. Montero, T. Dagnac, A.M. Carro

PSA-11 **$Fe_3O_4/SiO_2/TiO_2$ Nanocomposite for Magnetic Solid-Phase Extraction of Pharmaceuticals: Sorption and Desorption Study with MIP Application**
D. Mutavdžić Pavlović, K. Tolić Čop, D. Bakšić, I. Gabelica

PSA-12 **Capsule Phase Microextraction Combined with Gas Chromatography-Tandem Mass Spectrometry for the Determination of Polychlorinated Biphenyls in Water Samples**
N. Manousi, G. Efstratiadis, A. Kabir, K. Furton, E. Rosenberg, G. Zachariadis, N.P. Kalogiouri

PSA-13 **Ultrasound-Assisted Emulsification Microextraction (USAEME) for the Sensitive Determination of Different Chemical Class Herbicides in Water**
S. Sóñora, A. Castiñeira-Landeira, T. Dagnac, M. Llompart

PSA-14 **Sorption Performance of Molecularly Imprinted Polymer for the Selective Extraction of Sulfamethoxazole**
K. Tolić Čop, D. Mutavdžić Pavlović, I. Čolo

PSA-15 **Fabric Phase Extraction Empowered by the Use of Molecularly Imprinted Polymers for the Highly Selective Isolation of BPA from Water Samples analyzed by HPLC-DAD**
N.P. Kalogiouri, E. Pantazi, A. Konstantinou, A. Kabir, K. Furton, V.F. Samanidou

PSA-16 **A Magnet-Integrated Fabric Phase Sorptive Extraction Protocol as a Front-End to GC-MS/MS for the Trace Determination of Polycyclic Aromatic Hydrocarbons in Water Samples**
N.P. Kalogiouri, N. Manousi, A. Beina, A. Kabir, K. Furton, E. Rosenberg, G. Zachariadis

PSA-17 **Extraction of Phenolic Compounds from Olive Pomace Using Supramolecular Deep Eutectic Solvent**
G. Pietrangeli, S. Della Posta, C. Maggi, C. Fanali

PSA-18 **β-Cyclodextrin and Levulinic Acid Based Supramolecular Deep Eutectic Solvent: Characterization and Applications for the Extraction of Bioactive Molecules**
V. Terrigno, S. Della Posta, C. Fanali

PSA-19 **β-Cyclodextrins - Coated Magnetic Nanoparticles: Synthesis, Characterization, and Adsorption Studies**
M.C. Frondaroli, S. Della Posta, C. Fanali

PSA-20 **The Solvent-Assisted Dispersive Solid-Phase Extraction for Determination of Anionic Surfactant with UV-Vis Detection**
S. Zaruba, V. Andruch

PSA-21 **Vial-Coated Thin Film Microextraction for Perfluorinated Carboxylic Acids (PFCAs) Determination in Water Samples by GC-MS**
J.M. Luna-Díaz, L. Ferrer, L.O. Leal-Quezada, E. Palacio

PSA-22 **Modern Trends in Pre-Analysis in Clinical Research and Routine Practice**
L. Kujovská Krčmová, Ch. Suwanvecho, N. Přívratská, D. Turoňová, L. Matysová, V. Blaha

PSA-23 **Preconcentration of Bromide and Bromate by In-Vessel Headspace Liquid-Phase Microextraction Followed by Their Spectrophotometric Determination**
A. Vishnikin, A.-E. Tamen, Y. Bazel

PSA-24 **Untargeted Metabolomics for Monitoring Sinularia Soft Coral Response to Elevated Sea Temperature**
N.M. Hegazi, M. Emam, T. Mohamed, M. Al-Hammady, M. Hegazy, H. Gross

PSA-25 **Optimized Liquid-Liquid Extraction Method for the Determination of Buprenorphine and Its Main Metabolite in Commercial Plasma Using HPLC-UV**
M. Gumustas, C.H. Bozmaoglu, K.C. Tok, H.S.Suzen

PSA-26 **Rapid Methods for Determining the Total Content of Jet Fuel in Soil for Forensic Environmental Studies**
M. Alimzhanova, B. Abdykarimov, M. Mamedova, A. Suleime

PSA-28 **A Survey of Total Selenium in Soil, Maize Plants, and Maize Flour by Inductively Coupled Plasma Tandem Mass Spectrometry (ICP-MS/MS): A Case Study for South Africa**
N. Takata, A. Botha, P.N. Nomngong

Poster Session B

Monday, 16th September | 14:20-15:00

PSB-01 **Quantitation of Intact Proteins in Biological Fluids Using CZE-MS with Off-Line Microelution SPE Sample Pretreatment**
M. Opetová, R. Tomašovský, P. Mikuš, K. Maráková

PSB-02 **Targeted UPLC-ESI QQQ MS/MS Analysis of Bile Acids in Saliva and Gastric Juice: A Possibility for Early Non-Invasive Diagnosis of Barrett's Oesophagus**
M. Laštovičková, P. Itterheimová, V. Dosedělová, P. Kubáň, Š. Konečný, J. Dolina

PSB-03 **One Step Derivatization and Switchable Hydrophilic Solvent Microextraction for the Determination of Adamantine Analogues in Human Urine by HPLC-FLD**
M. Ntorkou, P.D. Tzanavaras, C.K. Zacharis

PSB-04 **A Green Liquid Phase Microextraction Using Phthalic Acid as Switchable Hydrophilicity Solvent for the HPLC Determination of Sildenafil in Human Urine**
M. Ntorkou, A. Doumtsi, S. Solomou, B. A. Gontad, P.D. Tzanavaras, C.K. Zacharis

PSB-05 **Dispersive Pipette Tips Extraction for Vitamin K Analysis**
N. Přívratská, Ch. Suwanvecho, D. Turoňová, L. Kujovská Krčmová

PSB-06 **Blood Microsampling Devices in Global Untargeted Metabolic Profiling**
D.M.S. Silva, M. Thaitumu, G. Theodoridis, P. Louail, J. Rainer, H. Gika

PSB-07 **Dried Blood Spot Devices: Precise, Convenient, and Patient-Friendly Devices for Analysis of Vitamin A and E**
Ch. Suwanvecho, N. Přívratská, D. Turoňová, L. Kujovská Krčmová

PSB-08 **Modernizing Diagnostics: Efficient Routine Vitamin K Analysis with a Focus on Metabolic Disorders**
D. Turoňová, K. Mrštná, Ch. Suwanvecho, N. Přívratská, L. Kujovská Krčmová

PSB-09 **Analysis of Biothiols in Non-Invasive Samples by Capillary Electrophoresis with Laser Induced Fluorescence and Amine Group Derivatization**
J. Volanek, P. Itterheimova, P. Kuban

PSB-10 **Investigation of Biologically Active Components from Karau Eryngium (Eryngium Karatavicum Iljin)**
N. Meirbekov, M. Sergazina, Y. Syrgabek, Y. Saltanat, M. Alimzhanova

PSB-11 **Geographical Origin Authentication of Cretan Thyme Honey Using Vacuum-Assisted Headspace Solid-Phase Microextraction Arrow**
A. Pateraki, E. Psillakis

PSB-12 **Enhancing Oxidative Stability Analysis in Adult Nutrition Formulas Using Microextraction Techniques and GC-MS**
A.M. Carro, J.A. Custodio-Mendoza, A.R. Silva

PSB-13 **Bisphenols Content in Mussel as Sentinel of Surface Sea Waters Coming from Galician Rías**
N. Carro, A. Portela, J. Cobas, I. García, A. Mouteira, M. Ignacio

PSB-14 **Fast HPLC-UV for Total Amino Acid Determination through Ultrasound-Accelerated Acid Hydrolysis**
J.A. Custodio-Mendoza, M.A. Kurek, P. Pokorski

PSB-15 **Comparison of Microwave-Assisted Saponification and Extraction Methods for MOH Determination in Meat**
D. Ferrara, P. Albendea, G. Purcaro

PSB-16 **Aptamer-Modified Magnetic Nanoparticles for Extraction of Milk Protein Allergen α-Lactalbumin from Foodstuffs**
M.J. Lerma-García, R. Mínguez-Peláez, N. Piqueras-García, M. Vergara-Barberán, J.M. Herrero-Martínez

PSB-17 **Design and Application of a 3D-Printed Device Coated with Solid-Phase Extraction Resins: An Alternative to QuEChERS for Extraction and Quantification of Five Pesticide Residues in Honey Samples via UHPLC-UV**
D. Lupu, G. Hancu, L. Ferrer

PSB-18 **Development of a Direct Liquid-Liquid Extraction Method Combined with UHPLC- DAD for the Determination of Seven Flavonoids in Extra Virgin Olive Oil**
E. Palacio, L. Bonilla, T.S. Sammani, L. Ferrer

PSB-19 **Improving Juice Processing Quality and Efficiency with a Novel Pectin Lyase**
M. Pavlović, M. Ristović, N. Drulović, M. Šokarda Slavić, Z. Vujčić, A. Margetić, S. Stojanović

PSB-20 **Extraction and Determination of Steroid Saponins in Tribulus Terrestris Nutraceuticals with Validated UHPLC-CAD Method**
M. Sanderová, D. Šatínský

PSB-21 **Plant-Based and Same Great Taste? Finding Off-Flavours Causing Negative Consumer Perception of Pea Milk Using High Capacity Sorptive Extraction (HiSorb)**
M. Santoro, L. Hearn, J.P. Mayser, R. Szafnauer

PSB-22 **Enzymatic Production and HPLC-RID Analysis of Prebiotic Oligosaccharides in Functional Foods**
S. Stojanović, M. Ristović, M. Pavlović, B. Dojnov, N. Božić, Z. Vujčić, A. Margetić

PSB-23 **Rapid Analysis of Phenolic Compounds in Plant-Based Milk Alternatives: A Smartphone-Based Approach**
M. Tobiszewski, L.A. Yahya, C. Vakh

PSB-24 **Influence of Grape Pomace Addition on the Nutritional and Functional Value of Maize Extrudates**
M. Ungureanu-Iuga, S. Mironeasa, A. Batariuc, C. Mironeasa

PSB-25 **Compliance with Current Regulations on Allergens and Hazardous Compounds in Hydroalcoholic Gels**
A. Castiñeira-Landeira, L. Vazquez, T. Dagnac, M. Celeiro, M. Llompart

PSB-26 **Metabolome Diversity of Nine Apiaceae Fruits and their Anti-Cellulite Potential**
N.M. Hegazi, M.A. Salem, H.H. Saad, N.M. Aborehab, M.H. El Bishbishy, S.M. Ezzat

PSB-27 **Synthesis and Characterization of Aptamer-Modified Hybrid-Silica Monolithic Capillary for Extraction of Amyloid Peptides**
A. Combès, I.D. Souza, M.E.C. Queiroz, V. Pichon

Poster Session C

Tuesday, 17th September | 10:50-11:30

PSC-01 **Voltammetric Procedure for the Determination of Ce(III) in Environmental Waters Utilizing Accumulation on an Multi-Walled Carbon Nanotubes Modified Screen-Printed Electrode**
M. Grabarczyk, M. Fialek, E. Wlazlowska

PSC-02 **Cathodic Stripping Voltammetry Using a Solid Bismuth Microelectrode for the Determination of Trace Amounts of Se(IV) in Environmental Water**
M. Grabarczyk, M. Fialek, C. Wardak

PSC-03 **A Synergistic Approach for the Co-production of Hydrogen and Nanocarbon from Plastic Waste via Thermo-catalytic Route**
A. Rafey, E. Ahmad, K.K. Pant, S. Upadhyayula

PSC-04 **Development of Analytical Green Methodologies for The Detection of Contaminants of Emerging Concern**
M.A. Andino-Enríquez, S. Taglianetti, D. Fabbri, C. Medana, F. dal Bello, P. Calza

PSC-05 **Sustainable Biocatalysis: Exploiting Hemp Waste for Lipase Immobilization and Oleic Acid Esterification**
V. Chiappini, D. Casbarra, M.L. Astolfi, A.M. Girelli

PSC-06 **Solvent-Free Reactions as a Key to the Synthesis of Organoboron Compounds**
G. Hreczycho, K. Kuciński, H. Stachowiak-Dłużyńska

PSC-07 **Reusing and Recycling 3D Printed Devices Coated with Solid-Phase Extraction Resin for Extraction of Antidepressants in Water: Towards a Truly Sustainability**
B. Mejía, L.O. Leal, L. Ferrer

PSC-08 **Comparison of Official Analytical Methods with Corresponding Methods Using SPME for Their Greenness**
F. Michel

PSC-09 **Simple and Rapid Determination of Salivary Lysozyme in Real Samples by tITP-CZE-UV**
R. Tomašovský, M. Opetová, P. Mikuš, K. Maráková

PSC-10 **Microflow LC-MS: A Step Towards Reconciling the Reduction of Environmental Impact and Analytical Performances in the Context of Green Chromatography**
L. Durand, B. Giroud, L. Wiest, E. Vulliet

PSC-11 **Utilization of Caffeine as a Potential Enhancer for Heat Transfer Fluids**
J. Panić, N. Cako Bagány, S. Papović, T.T. Borović, A. Vukov, S. Belić, S. Gadžurić, M. Vraneš

PSC-12 **An Updated Gradient PLE-SPE×HPLC-PDA System for Extraction, Fractionation, and Analysis of Valuable Compounds from Cocoa Bean Shells**
F.S. Bragagnolo, M.M. Strieder, V.L. Sanches, M. Gonzalez-Miquel, M.A. Rostagno

PSC-13 **Introduction of High Performance Liquid Chromatography coupled to Zone Fluidics as a Versatile Approach for Derivatization Reactions**
A. Tsiasioti, C. K. Zacharis, P. D. Tzanavaras

PSC-14 **Pulsed – Post Column Derivatization Coupled to High Performance Liquid Chromatography: A new Concept to Minimize the Reagent Consumption**

A. Tsiasioti, P.D. Tzanavaras

PSC-15 **On Site Analytical Strategies to Monitor Organic and Inorganic Pollutants in Fish Farms**
P. Calza, F. Cristaudo, M.A. Andino-Enríquez, M. Tramontini, D. Fabbri, P. Inaudi, A. Giacomino

PSC-16 **In-Situ Arsenic(III) Colorimetric Detection Exploiting Hydride Generation and Metal Organic Framework Ag-BTC Integrated in a 3D-Printed Millifluidic Device**
L. Maza, M.A. Vargas-Muñoz, L. Ferrer, E. Palacio

PSC-17 **Lab-on-Paper Colorimetric Device for Extraction-Free Phenolic Fraction Evaluation in Olive Oil**
A. Scroccarello, F. Della Pelle, I.V. Di Cristoforo, M. Del Carlo, D. Compagnone

PSC-18 **Europium-Based Luminescent Metal-Organic Framework (Eu-MOF) Immobilized on a 3D-Printed Device as a Multisample Fluorescent Sensor for In-Situ Smartphone-Assisted-Detection of Tetracyclines in Water Samples**
M.A. Vargas-Muñoz, G. Turnes, L. Ferrer, E. Palacio

PSC-19 **Electrochemical Sensor Manufactured on Algae-Paper Equipped with Nanobiochar from By-products for Bisphenol-A Determination in Zebrafish Embryo Model**
F. Della Pelle, F. Silveri, A. Scroccarello, C. Merola, R.Cancelliere, L. Micheli, D. Compagnone

PSC-20 **Automated Preparation of Multi Compound Calibration Standards According to SANTE Requirements**
H.-J. Huebschmann, T. Breski

PSC-21 **Whey Proteins as a Source of Essential Minerals Evaluation of More Environmentally Friendly Analytical Methods**
J. Jablan, E. Margui, B. Bilandzija, L Budic, T. Videkovic

PSC-22 **Catalysis of [3+2] Cycloadditions by Acetic Acid Using Microwaves or Ultrasound**
I. Damljanović, J. Bugarinović, D. Stevanović, M. Pešić

PSC-23 **Audio-Tactile Pictures for Teaching Spectrometry to Individuals with Visual Impairments Towards Accessibility**
V. Samanidou, N. Manousi, N. Kalogiouri, L. Isaraj, E. Chronopoulou, K. Papadopoulos

PSC-24 **Advancements in Electrolyte Modification for Enhanced Safety and Sustainability in Lithium-Ion Batteries**
N. Cakó Bagány, J. Panić, T.T. Borović, S. Papović

PSC-25 **Natural Deep Eutectic Mixture as Environmentally Friendly Solvent for Pharmaceutically Active Ionic Liquid**
N. Cako Bagány, J. Panić, S. Papović, T.T. Borović, A. Vukov, S. Belić, S. Gadžurić, M. Vraneš

PSC-26 **SERS-Based Sandwich Immunoassay Platform for Non-Invasive Determination of IgG**
A. Gumustas, H. Torul, M. K. Ulku, M.A.S. Arikan, U. Tamer, E. Yildirim

PSC-27 **Polydopamine-Coated Steel Wire: Thin Film Microextraction Methodology for Diazepam and Nordazepam Detection**
K.C. Tok, T. Karasu, C.H. Bozmaoglu, L. Uzun, M. Gumustas

PSC-28 **Vacuum-Assisted Headspace Solid-Phase Microextraction Analysis of Energy Drinks**
Y. Syrgabek, M. Alimzhanova

Poster Session D

Tuesday, 17th September | 14:20-15:00

PSD-01 **Molecularly Imprinted Polymer-Coated Toothpicks for the Determination of Diazepam and Major Metabolite**
C.H. Bozmaoglu, T. Karasu, K. Can Tok, L. Uzun, M. Gumustas

PSD-02 **Supported Liquid Extraction Using Wetted Nanofibrous Discs as a Simple Approach for In Vial Extraction Prior to Chromatography Analysis**
E. Czyz, D. Šatínský

PSD-03 **Upcycling Plastic Wastes as Supports for Preparation of Metal-Organic Framework-Based Sorbents**
J.M. Herrero-Martínez, M.A. Martínez-Briones, M. Vergara-Barberán, M. Beneito-Cambra, E.F. Simó-Alfonso, M.J. Lerma-García

PSD-04 **Core Shell Particles with Strong Cationic Exchange Moieties as Selective Material**
R.M. Marcé, A. Moral, F. Borrull, P.A.G. Cormack, N. Fontanals

PSD-05 **A Novel Automatic Flow-Batch Liquid-Liquid Microextraction Lab-in-Syringe Platform Based on Natural Deep Eutectic Solvents for Toxic Metal Determination**
N. Manousi, V. Christoforou, C.K. Zacharis, A. Anthemidis

PSD-06 **Evaluation of Metals Leachability from 3D Printed Analytical Devices**
E. Palacio, A. Figuerola, M. Marí, L. Ferrer

PSD-07 **Polyvinyl Chloride Coated Paper Post-Modified with Diphenylamine: A Sustainable Sorptive Phase to Extract Opioids from Saliva Samples**
A. Pedraza-Soto, C. Calero-Cañuelo, R. Lucena, S. Cárdenas

PSD-08 **Strong Cation Exchange Microparticles Immobilized on Paper for the Selective Isolation of Opioids in Biofluids**
A. Pedraza-Soto, R. Lucena, S. Cárdenas

PSD-09 **Use of Waste Plastics as Selective Supports for the Analysis of Cow's Milk Allergens**
M. Vergara-Barberán, I.F. Colonescu, T. González-Sanz, M. Beneito-Cambra, M.J. Lerma-García, J.M. Herrero-Martínez

PSD-10 **Development of an Affinity Sorbent in a Paper-Based Device for Lysozyme Extraction in Foods**
M.J. Lerma-García, N. Piqueras-García, M. Vergara-Barberán, J.M. Herrero-Martínez

PSD-11 **Identification of Organic Compounds Released from 3D Printed Devices by GC-MS**
B. Mejía, A. Figuerola, L. Ferrer, E. Palacio

PSD-12 **Comprehensive Analysis of Volatile Carbonyl Compounds in Wood-Based Panels Through Gas-Diffusion Microextraction Combined with HPLC-DAD**
R.M. Ramos, F.D. Gonçalves, M.L. Almeida, J.M. Martins, L.H. Carvalho, J.A. Rodrigues

PSD-13 **Development of Low-Cost Extraction Platforms Modified with Metal-Organic Frameworks for the Analysis of Emerging Pollutants**
M. Vergara-Barberán, M.Á. Martínez-Briones, M.J. Lerma-García, J.M. Herrero-Martínez

PSD-14 **GC×GC Analysis of Organics Leached from Cigarettes and Heat-not-Burn Tobacco Products**
I. Kandylioti, E. Psillakis

PSD-15 **Green Multi-Residue Pesticide Extraction from Food Samples Using Natural Deep Eutectic Solvents**
L. Carbonell-Rozas, I. Aloisi, L. Righetti, A. Garrido Frenich, H. Mol

PSD-16 **Hydrocarbon Oil Index: Scale Down Approach for Automation of C10-C40 According to UNI EN ISO 9377-2**
A. Carretta

PSD-17 **Developing Preanalytical Method for the Extraction and Preconcentration of Non-Steroidal Anti-Inflammatory Drugs from Wastewater Samples Using Ionic Liquid-Based Aqueous Biphasic Systems**
A. Dimitrijević, A. Jocić, S. Marić, D. Tekić, J. Mušović

PSD-18 **In-Syringe Dispersive Solid Phase Extraction of Selected Alkyl-Phenols Coupled Online to HPLC**
T.T.M. Htet, B. Horstkotte, H. Sklenářová

PSD-19 **New Developments for MOSH/MOAH Automated Analysis**
H.-J. Huebschmann, T. Uber

PSD-20 **Green Approach Strategy Using Aqueous Biphasic Systems with Ionic Liquids as Pre-Treatment Method for Pesticide Determination in Food Sample**
A. Jocić, S. Marić, D. Tekić, J. Mušović, A. Dimitrijević

PSD-21 **Green Extraction of Pesticides in Pear by Matrix Solid Phase Dispersion combined with Natural Deep Eutectic Solvents**
A. Martín-Esteban, E. Miguel, A.I. García-Valcárcel

PSD-22 **A Composite Cryogel Embedded in a Needle Hub for Miniaturized In-Syringe Solid Phase Extraction of Preservatives in Beverage Samples Followed by HPLC-DAD Analysis**
P. Nurerk, O. Bunkoed, J. Sapphanachai

PSD-23 **Experimental Design and Optimization of the Fabric Phase Sorptive Extraction of Anti-Diabetic Drugs in Water**
A. Misolas, M. Sleiman, V. Sakkas

PSD-24 **3D Printed Device for In-Situ Solid-Phase Extraction of Six NSAIDs from Wastewater and Subsequent Analysis by UPLC-DAD/FLD**
C. Castro-García, R. Rodríguez-Maese, L.O. Leal-Quezada, E. Palacio, L. Ferrer

PSD-25 **Activated Carbon from Grapefruit Peel as Sorbent Phase for Microextraction Technologies**
P. Richter, A. Molina-Balmaceda, V. Rojas-Candia, J.J. Triviño, D. Arismendi

PSD-26 **Development of a Fluidic Platform for Easy Monitoring of Superoxide Anions**
F.A. Casado-Carmona, L. Garcia-Moll, M. Galián-Salas, M. Oliver, M. Miró

PSD-27 **Extraction of Terbinafine from Poly(lactic-co-glycolic Acid) Based Solid Dispersions Prior to Its Determination by Fast, Sensitive UHPLC-DAD Method**
L. Matysová, K. Mrštná, K. Matoušová, P. Matouš, L. Kujovská Krčmová, F. Švec

PSD-28 **Development of Novel Adsorbents for Extraction and Analysis of Lithium from Reverse Osmosis Brine**
S.F.Y. Li

5. Plenary Presentations

Microplastics in the Environment: Analytical Chemistry Methods, Sorption Material, Risks and Sustainable Solutions

PL-01

D. Barceló[1,2].
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Keywords: *Analysis, Microplastics, Risks, Sorption, Sustainability*

Plastic pollution is nowadays a global and ubiquitous problem everywhere: marine environment, sand beaches, wastewaters, surface waters, soils, sludges, sediments, biota, food and air. Plastic is part of our daily life and worldwide we use 4 trillion plastic bags annually and 1 million plastic bottles every minute. Microplastics (MPs) are directly released into the water or formed by degradation of Macroplastics. Plastic litter enters the marine environment from diverse points and diffuse sources and it can be transported through rivers long distances before being deposited in the bottom of seas. Few studies suggest that river litter can contribute up to 40% of all marine litter input, being estimated over 1.2-2.5 million tonnes of plastic every year [1,2]. MPs amount in soils globally is estimated between 1.5 to 6.6 Million Tons, being China with 660 KiloTons of MPs in soils the number one in the list. The main reason has been attributed to the irrigation of the agricultural fields with wastewater. The estimation of MPs in soils of Spain and Italy is 38 and 28 KiloTons respectively due to the increasing reuse of water for agriculture as a consequence of water scarcity in the Mediterranean region. The total amount of MPs present in soils and solid organic wastes around the globe is probably higher than the amount of MPs present in the surface of the oceans [2,3]. MPs, as many other contaminants, can percolate through the agricultural soils and reach the groundwater table [4]. Having said that, this presentation will cover in the first part different aspects of MPs and MacroPlastic litter pollution in terrestrial environment as well coastal waters, rivers, sediments and lakes. Case studies of MPs pollution in several coastal environments, sediments and catchments of China, Saudi Arabia, India, Europe and Australia will be reported [2,5,6]. The second part of this lecture will discuss Green Analytical Chemistry (GAC) protocols for the analysis of MPs in water [7] as well as applied to ecotoxicology [8]. GAC issues will be discussed in all steps of the method (i) sampling, (ii) sample preparation and (iii) identification and quantification measures can be taken to make the method more environmentally friendly and sustainable, safer for the operator by assessing their greenness through Analytical Eco-scaleand AGREE metrics among others [7]. In-vitro and in-silico ecotoxicological methodologies are proposed instead the use of fishes and vertebrates in general [8]. The following part of this lecture will describe as well MPs as vectors of pharmaceuticals such as non-steroidal anti-inflammatory drugs (NSAIDs) or, psychiatric drugs that can sorb to MPs surface [9]. Lastly, it is expected that MPs will affect communities, biological diversity, and ecosystem processes [10]. As regards to toxicity of MPs that is expected, smaller MPs and NPs particles will be more toxic to organisms. Many aquatic organisms are used for biomonitoring programs being possible to obtain quantitative information about the state of health of the ecosystem. Bivalves such as *Mytilusgalloprovincialis*were used [11]. This is part of the so called “mussel-watch” program for MPs but we will mention its presence and effects in lakes too [12]. To this end I would like to highlight few recommendations to mitigate plastic pollution: (i) law and waste management strategies, such as exploring new removal technologies and avoid landfilling (ii) more education, outreach and awareness, (iii) increasing monitoring and risk assessment to better understand the threat to biodiversity and (iv) further innovative research lines like the development of bioplastics to replace single use plastics (SUPs). In short MPs and MacroPlastics need the involvement of the scientific community, stakeholders, plastic producers and politicians to minimize the global risk.

References

[1] D. Barcelo, Y. Picó, Case Stud. Chem. Environ Eng., 2 (2020) 100019.
[2] B. Zhou et al., J. Haz. Mat., 368 (2020) 121814.
[3] Y. Zhou, et al., J. Haz. Mat., 445 (2023) 130596.
[4] J. Cha, J.-Y. Lee, R.W. Chia, Sci. Total Environ., 864 (2023) 161027.
[5] G.F. Schirinzi et al., Sci. Total Environ., 714 (2020) 136807.
[6] Y. Picó, V. Soursou, A.H. Alfarhan, M.A. El-Sheikh, D. Barceló, J. Haz. Mat., 416 (2021) 125747.
[7] D. Barcelo, Y. Picó, Curr. Opin. Green Sustain. Chem., 31 (2021) 100503.
[8] P. Pastorino, M. Prearo, D. Barcelo, Green Anal. Chem., 81 (2024) 100096
[9] L.H.M.LM. Santos, S. Rodriguez-Mozaz and D. Barceló, Case Stud. Chem. Environ Eng.,3 (2021) 100079.
[10] E. Agathokleous, I. Iavicoli, D. Barceló, Edward J. Calabrese, J. Haz. Mat., 417 (2021) 126035.
[11] F. Frovenza, et al., Ecol. Indic., 142 (2022) 109212.
[**12]** P. Pastorino, et al., Ecol. Indic., 150 (2023) 110215.

Deep Eutectic Solvents: A Green Approach to the Analysis of Organic Pollutants in Complex Foodstuffs

PL-02

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Keywords: *Deep eutectic solvents, Food analysis, Green sample preparation, Green solvents, Organic pollutants*

Deep eutectic solvents (DESs) were developed at the beginning of the 2000s' as a novel category of green solvents alternative to ionic liquids (ILs) [1]. DESs shared many of the positive features of ILs, namely negligible volatility, high thermal and chemical stability, and reduced flammability over a relatively wide range of temperatures. However, their synthesis was cheaper, easier, did not generate residues or by-products, and they were considered less toxic than ILs [1]. In consequence, DESs immediately attracted the attention of researchers, who rapidly started to evaluate their potential as green solvents in different study areas, in particular in the food and pharmaceutical fields [2]. Concerns regarding the toxicity of some of these mixtures made researchers to switch to natural components to prepare DESs. The term "natural (deep) eutectic solvents", NA(D)ESs, was introduced in 2011 by Choi et al. [3] to denote (D)ESs synthesized from cellular components, such as alcohols, sugars, organic acids, amino acids and choline derivatives. The natural origin of these components, in principle, sufficed to ensure the safety, biocompatibility and biodegradation capability of the resulting mixtures. Therefore, NA(D)ESs were also assumed to fulfil the principles of Green Analytical Chemistry (GAC) [3] and Green Sample Preparation [4] and, similarly to that observed for DESs, they have also been evaluated as alternative green solvents in a variety of application studies. Up to now, a large majority of the studies involving (NA)DESs have focused on the recovery of relatively concentrated metal ions, polar compounds and bioactives from natural sources, in many instances in combination with miniaturized extraction techniques [5]. However, applications dealing with the extraction of analytes at residue level from particularly complex matrices, such as fat-containing foodstuffs, are much more limited in the literature.

In this communication, an application study involving (NA)DES for the treatment of fatty foodstuffs will be used to illustrate how the tunable properties and selectivities of these green solvents can be used for the extraction and isolation of regulated trace organic contaminants from these complex matrices. Benefices and limitations of (NA)DES-based sample preparation methodologies as well as remaining issues in this particular application area and possible lines of future development will also be discussed.

Acknowledgements
This work is part of the I+D+i project PID2019-106405GB-I00 financed by MCIN/ AEI/10.13039/501100011033. Authors thank the Comunidad of Madrid and European funding from FSE and FEDER programs for financial support (project S2018/BAA-4393, AVANSECAL-II-CM).

References

[1] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Novel solvent properties of choline chloride/urea mixtures, Chem. Commun. 99 (2003) 70–71.
[2] D.O. Abranches, J.A.P. Coutinho, Everything you wanted to know about deep eutectic solvents but were afraid to be told, Annu. Rev. Chem. Biomol. Eng. 14 (2023) 141-163
[3] A. Gałuszka, Z. Migaszewski, J. Namieśnik, The 12 principles of Green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices, TRAC Trends Anal. Chem. 50 (2013) 78-84.
[4] A.I. López-Lorente, F. Pena-Pereira, S. Pedersen-Bjergaard, V.G. Zuin, S.A. Ozkan, E. Psillakis, The ten principles of green sample preparation, TRAC Trends Anal. Chem. 148 (2022) 116530.
[5] J. Bintanel-Cenis, M.A. Fernández, B. Gómara and L. Ramos. Critical overview on the use of hydrophobic (deep) eutectic solvents for the extraction of organic pollutants in complex matrices. Talanta 270C (2024) 125599.

Progresses in the Foodomics Study of Natural Green Extracts Against Alzheimer's Disease

PL-03

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Keywords: *Alzheimer disease, Foodomics, Green extraction, Lipidomics, Metabolomics, Natural products*

Alzheimer's disease (AD), the most common form of dementia, is a multifactorial pathophysiology characterized by neuroinflammation, extensive oxidative damage, synaptic loss and neuronal cell death. However, only very few drugs have been approved for the treatment of some AD symptoms, although it is well known that not cure has been found so far. As a result, new strategies are urgently required, and among them, several studies have suggested that natural products can be worthy to investigate.

In this work, many natural sources of potential bioactive compounds have been investigated, and based on several green extraction processes and in-vitro approaches, we found terpenoids and carotenoids to have neuroprotective potential. In addition, the neuroprotective activity of these natural extracts is confirmed in a neuronal cell culture model as well as their low toxicity. Moreover, these extracts show very good neuroprotective activity in-vivo using a transgenic Caenorhabditis elegans as AD model. Lipidomics (using CSH-QTOF MS/MS), combined with transcriptomics (using NGS methods) and metabolomics (using HILIC-QTOF MS/MS and GC-QTOF-MS/MS) are applied following a Foodomics approach to investigate the effect of the best neuroprotective candidates on the transgenic C. elegans.

Acknowledgements
This research was funded by the Ministry of Science and Innovation (MCI), Spain, PID2020-113050RB-I00 project.

Electromembrane Extraction – Quo vadis

PL-04

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Keywords: *Electromembrane extraction, Microextraction, Sample preparation*

Electromembrane extraction (EME) is a microextraction technique for bases, acids, and ionic compounds [1]. The principle of EME, and commercial equipment, are illustrated in **Figure 1**. EME involves extraction from an aqueous sample, across a liquid membrane and into an aqueous acceptor under the influence of an external electric field. The liquid membrane is a 2-10 µL-volume of organic solvent (membrane solvent) immobilized by capillary forces in the pores of a polymeric support membrane. The membrane solvent is immiscible with water, and therefore the liquid membrane is stable during extraction. The acceptor is a pure aqueous buffer solution. More than 500 papers have been published on EME, using homebuilt equipment. This includes EME in 96-well configuration and in microfluidic systems. EME was commercialized recently [2], based on vials produced in conducting polymer. In this system, the vials are used both as electrodes and containers for the sample and acceptor.

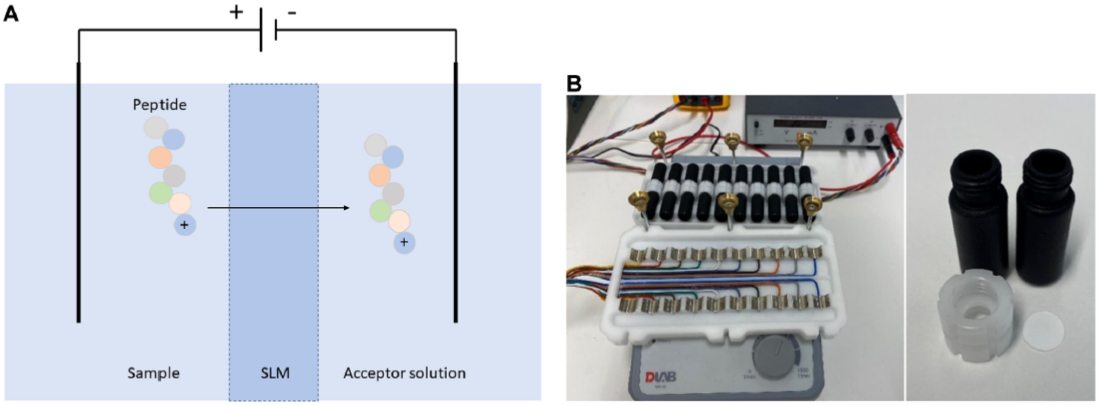

Figure 1. Principle and commercial equipment for electromembrane extraction

The mass transfer in EME is controlled by the external electrical field. The cathode (negative electrode) is located in the acceptor for extraction of bases, and the anode (positive electrode) is located in the sample. The sample and the acceptor are kept at neutral or acidic pH, and basic analytes are extracted as protonated species (cations). For acids, the polarity is reversed, and the sample and the acceptor are at neutral or alkaline pH. In such way, acids are extracted as anions.
The selectivity in EME is controlled by the chemical composition of the liquid membrane, the direction and magnitude of the electrical field, and by pH in the sample and acceptor. Due to high selectivity, EME provides efficient sample cleanup from complex environmental samples, biological fluids, and samples of food and beverages. Sample volumes are typically in the range 0.05-10 mL, and EME may provide substantial pre-concentration. Since the acceptors are aqueous, there is no need for evaporation and reconstitution, and they can be analyzed directly with instrumental techniques such as LC-MS. Finally, EME is green, and the consumption of organic solvent is below 10 µL per sample.
This presentation will give an overview of EME, with focus on principles, analytical performance, advantages, limitations, and method development. In addition, the potential of EME and future directions will be discussed.

References

[1] S. Pedersen-Bjergaard, K. E. Rasmussen, Electrokinetic Migration across Artificial Liquid Membranes – New concept for Rapid Sample Preparation of Biological Fluids, *Journal of Chromatography A* 1109 (2006) 291-307.
[2] M. Drobnjak, F. Hansen, E. Leere Øiestad, T. Løvli, R. Trones, Ø.G. Martinsen, S. Pedersen-Bjergaard, Electromembrane extraction with vials of conducting polymer, *LCGC North America* 38 (2020) 435-439.

6. Keynote Presentations

Leveraging Plastic's Potential in Sample Preparation

KN-1

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Keywords: *Plastic waste, Plastic recycling, 3D Printing, Thermoplastics, Sorbents*

Plastics have become the most popular and ubiquitous material in our daily lives, and global plastic production has increased significantly in the last decades [1]. However, the exponential increase in the manufacture of disposable plastic goods has overwhelmed the world's ability to handle them properly, and plastic pollution has become one of the most urgent environmental issues of the 21st century. To address pollution concerns, strategies for recycling/recovery/management of plastic waste [2] are crucial; however, globally, only 9% of plastic waste was recycled in 2019 [3]. Additionally, only some plastics can be recycled, falling under the category of thermoplastics, such as PET (polyethylene terephthalate), HDPE (high-density polyethylene), LDPE (low-density polyethylene), PVC (polyvinyl chloride), PP (polypropylene), and PS (polystyrene). Given this scenario, upcycling of waste into valuable chemicals is of utmost interest and has garnered significant attention in recent years as a way to reduce plastic waste and promote the circular economy. Thus, these waste materials can be properly treated or chemically converted to produce high-value-added functional materials [2, 4]. For example, recycling PET into valuable materials via chemical depolymerization represents one of the most feasible recycling approaches, since it can generate building blocks for the synthesis of many valuable functional materials for different applications [4]. Another alternative that has been recently explored is the recycling of waste plastics through additive manufacturing, where 3D printing materials (filaments) can be reproduced from recycled plastics to produce 3D printed objects [5].

In this communication, we aim to showcase several strategies developed in our research group to recycle and reuse plastics generated (pipette tips, Falcon tubes, PET/HDPE containers, etc.) in analytical research laboratories to obtain supports/devices with valuable functional materials (polymer monoliths, metal-organic frameworks, aptamers, etc.) oriented towards sample preparation purposes.

Acknowledgements

This work was supported by the project (PID2021-125459OB-I00) funded by MCIN/AEI/10.13039/501100011033 and by "ERDF A way of making Europe" by the European Union, and the grant CIAICO/2022/183 funded by Generalitat Valenciana. Also, this study forms part of the Advanced Materials program and was supported by MCIN with funding from European Union Next Generation EU (PRTR-C17.I1) and by Generalitat Valenciana. Besides, the authors acknowledge the support of the Spanish Thematic Network on Sample Treatment (RED2022-134079-T).

References

[1] Plastics—The facts 2019. An Analysis of European Plastics Production, Demand and Waste Data (2019). https://www.plasticseurope.org/it/resources/publications/1804-plastics-facts-2019 (accessed 20 April 2024).

[2] A.A. Koelmans, N.H. Mohamed Nor, E. Hermsen, M. Kooi, S.M. Mintenig, J. De France, Microplastics in freshwaters and drinking water: critical review and assessment of data quality, Water Res. 155 (2019) 410–422.

[3] K. Ragaert, L. Delva, K. Van Geem, Mechanical and chemical recycling of solid plastic waste, Waste Manag. 69 (2017) 24–58.

[4] S. M. El-Sayed, D. Yuan, Waste to MOFs: sustainable linker, metal, and solvent sources for value-added MOF synthesis and applications, Green Chem. 22 (2020) 4082–4104.

[5] S. Singh, S. Ramakrishna, Recycling of thermoplastic wastes: a route of waste to wealth via three-dimensional printing, in: M.S.J. Hashmi (Ed.), Encyclopedia of Materials: Plastics and Polymers, Elsevier, New York, 2022, Vol. 1, pp. 510-515.

Nanofibers: Advanced Format of Orgaic Polymer-Based Materials for Sample Preparation in HPLC

KN-2

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Keywords: *Sample preparation, Solid phase extraction, Polymer, Fibers, Electrospinning*

Solid phase extraction (SPE) is one of the most popular sample preparation methods because it can significantly reduce the amount of interfering ballast compounds in the sample prior to analysis and matrix effects in MS detection. A large number of advanced sorbents suitable for SPE-HPLC and capable of purifying a variety of matrices includes among many other nanomaterials and, in particular, nanofibers [1,2]. Although various approaches can be used to prepare nanofibers, the relatively simple and inexpensive electrospinning is the most widely used. Electrospun fibers have already been applied in both off-line and on-line sample preparation by solid phase extraction while treating different types of matrices. Their advantages include affordability, the wide variability of chemistries of available polymers, and high extraction efficiency. We tested fibers prepared from fairly common polymers including poly(vinylidene difluoride), polystyrene, polyacrylonitrile, polyamide 6, poly(ε-caprolactone), poly(lactic acid), poly (ethylene imine), polyethylene, and polypropylene. Fibers made from these polymers encompass a wide range of adsorption mechanisms due to their different chemistries, hydrophobicity/hydrophilicity, acceptor/donor properties, dipole-dipole, and π-π interactions.

Our micro- and nanofibers were prepared by simple meltblowing, a combination of meltblowing and electrospinning, as well as DC and AC electrospinning techniques. We also developed a composite material in which robust meltblown fibers were used as a scaffold for more fragile, smaller diameter electrospun nanofibers. This approach increased the overall surface area and extraction capacity while maintaining the desired robustness. Alternatively, we have introduced modifications allowing to produce hybrid materials and coated fibers. For example, hybrid polymer fibers were prepared by dispersing particles, such as magnetic nanoparticles, graphene, activated carbon, and carbon black, into the polymer solution prior to electrospinning.

Surface modification of polymer nanofiber sorbents is another way to improve their performance by changing their functionalities. This was achieved by dip-coating, where the surface of polymer fibers was covered with polyhydroxy compounds including graphene oxide, tannin, dopamine, hesperidin, and heparin. The sorbents in free fibers format were packed in commercial stainless-steel cartridges and used for on-line SPE-HPLC. After testing fibers prepared from different electrospun polymers, those produced by the meltblown-co-electrospinning process of poly(ε-caprolactone) coated with graphene oxide provided the best matrix recovery of phenolic compounds from spiked river water and human plasma. Excellent analyte recoveries of 70–112% were achieved.

Alternatively, small 10 mm diameter nanofiber discs were cut from a compact and mechanically stable 1–2 mm thick micro/nanofiber mat. The best mat was prepared by the AC electrospinning of poly(ε-caprolactone) solution containing graphene nanoplates. Extraction was carried out in a stirred sample containing the disk located in a beaker. In another implementation, the disc was pierced with a steel staple wire, and placed in the sample. The magnetic stirrer rotated the disc at the bottom of the beaker and simultaneously stirred the liquid thus facilitating the adsorption. The off-line SPE using these discs was demonstrated with the extraction of compounds from local river water and its spiked counterpart. We determined typical contaminants of different polarities, including bisphenols A, C, S, Z, fenoxycarb, kadethrin, and deltamethrin. Compared to previous reports, our method allowed a significant reduction in sample preparation steps, which included only sorbent conditioning, adsorption, and final desorption directly in the HPLC vial. Very small amounts of sorbent and organic solvent were required for the extraction in the HPLC vial making our approach environmentally friendly with a method greenness of 0.61.

Acknowledgements

The authors gratefully acknowledge the Grant Agency of the Czech Republic (project GACR 23-05586 S) for financial support of the projects.

References

[1] M. Háková, L. Chocholoušová Havlíková, P. Solich, F. Svec, D. Šatínský, Electrospun nanofiber polymers as extraction phases in analytical chemistry – The advances of the last decade, TrAC Trends in Analytical Chemistry 110 (2019) 81-96.
[2] M. Najafi, M.W. Frey, Electrospun nanofibers for chemical separation, Nanomaterials 10(5) (2020) 982.

Advanced Extraction Techniques Followed by GC-MS/MS and LC-MS/MS for the Determination of Hazardous Chemicals from Tire Microplastics

KN-3

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Keywords: *Chromatography-mass spectrometry, Emerging pollutants, Extraction technologies, Microplastics, Tire crumb rubber*

Microplastic pollution is a main hot topic for many agencies and bodies such as the ECHA in Europe and the US EPA in America, being nowadays a concern for the general public. Tire wear particles produced incidentally by vehicles are the second source of microplastics reaching the environment. Crumb rubber from recycled and shredded end-of-life tires intentionally used in sports pitches and playgrounds is the first intended source of microplastics in the environment, being also a main issue for ECHA and other agencies [https://echa.europa.eu/hot-topics/granules-mulches-on-pitches-playgrounds].

This material is a complex mixture of hazardous chemicals, some of which are very well-known such as PAHs or heavy metals [1]. However, other emerging contaminants such as the p-phenylenediamines family (PPDs) have received little attention and only very recently emerged as environmentally hazardous substances [2,3].

In this talk, several analytical approaches focusing on the determination of tire related chemicals in crumb rubber and other matrices will be presented [3-5]. Examples of sample preparation including advance extraction and microextraction techniques in combination with LC-MS/MS and GC-MS/MS analysis will be provided. The application to a wide range of real samples will demonstrate the methods suitability, thereby contributing significantly to the knowledge of the global impact of recycled tire crumb rubber microplastics, both from an environmental and human health perspectives.

Acknowledgements

The authors thank projects PID2022-140148OB-I00, RED2022-134079-T and RETOSPID2019-104336RB-I00 (Ministry of Science, Innovation and Universities, Spain), ED431B 2023/04 and IN607B 2022/15 (Galician Competitive Research Groups, Xunta de Galicia). This study is also based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society. All these programs are co-funded by FEDER (UE)

References

[1] M. Celeiro, T. Dagnac, M. Llompart, Determination of priority and other hazardous substances in football fields of synthetic turf by gas chromatography-mass spectrometry: A health and environmental concern, Chemosphere 195 (2018) 201-211.

[2] Z. Tian, H. Zhao, K.T. Peter, M. Gonzalez, et al., A ubiquitous tire rubber–derived chemical induces acute mortality in coho salmon, Science 371(6525) (2021) 185-189**.**

[3] A. Duque-Villaverde, D. Armada, T. Dagnac, M. Llompart, Recycled tire rubber in the Spotlight. Determination of hazardous and lethal substances, Sci. Total Environ. 929 (2024) 172674.

[4] D. Armada, M. Celeiro, T. Dagnac, M. Llompart. Green methodology based on active air sampling followed by solid phase microextraction and gas chromatography-tandem mass spectrometry analysis to determine hazardous substances in different environments related to tire rubber, J. Chromatogr. A 1668 (2022) 462911.

[5] D. Armada, A. Martínez-Fernandez, M. Celeiro, T. Dagnac, M. Llompart, Sci. Total Environ. 857 (2023) 159485.

An Overview of Molecularly Imprinted Polymers for the Green Analysis of Pharmaceuticals by Electrochemical Sensing

KN-4

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Keywords: *Electochemical sensors, MIP sensors, Pharmaceuticals, Green assay*

Molecular imprinting technology is a creative method that enables synthetic biorecognition gaps to imitate real biological derivatives like antibodies, receptors, enzymes, etc. After removing the target analyte, synthetic cavities enable the recognition and selective rebinding of the template. In this case, molecular imprinting technology offers biosimilar receptors with higher specific affinities and better stability than natural receptors and biomolecules [1]. Although stable and durable MIPs seem relatively easy to create to achieve maximum efficiency, some optimization parameters should be considered, such as appropriate functional monomer and crosslinker and optimal ratios between functional monomer, template, and crosslinker [2]. The optimization process can vary based on the polymerization technique. In addition, the structure of the polymeric matrices and the type of bond contact between the template and the polymer are two important factors in MIPs. It was reported that template monomer interactions are realized through non-covalent interactions such as van der Waals forces, hydrogen bonds, and dipolar interactions [1, 2]. Among them, MIP-based electrochemical sensors have a significant place because, with MIPs, it is possible to overcome the lack of selectivity issue in electrochemical sensors.

MIP-based electrochemical sensors and miniature electrochemical transducers can detect target analytes in situ. Thanks to superior chemical and physical stability, low-cost manufacturing, high selectivity, and fast response, MIPs have recently become an interesting field. The increase in environmental awareness and stricter regulation for the use of chemicals and economic competitiveness are challenging the scientific community and industry to explore greener strategies in their processes, preventing pollution, and reducing waste while maximizing the efficiency of the processes, and that can only be achieved by the application of the green chemistry and engineering principles. Molecular imprinting has much to gain in applying these green tools since new alternative solvents and clean technologies, combined with computational tools, can optimize both the polymer and the process itself.

References

[1] L. Uzun, A.P.F. Turner, Molecularly-imprinted polymer sensors: realising their potential, Biosens. Bioelectron. 76 (2016) 131e144.
[2] K. Graniczkowska, M. Pütz, F.M. Hauser, S. De Saeger, N.V. Beloglazova, Capacitive sensing of N-formylamphetamine based on immobilized molecular imprinted polymers, Biosens. Bioelectron. 92 (2017) 741e747.

Deep Eutectic Solvents in Microextraction: Benefits and Limitations

KN-5

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Keywords: *Deep eutectic solvent, Liquid-phase microextraction, Natural deep eutectic solvent*

The 12 principles of Green Analytical Chemistry (GAC) were described by Galuszka et al. [1] based on the principles of Green Chemistry defined by Anastas and Warner [2]. The first principle of GAC is: "*Direct analytical techniques should be applied to avoid sample treatment*". However, analytical chemistry scientists know quite well that almost all of the samples need a treatment for different reasons (i.e., adaptation to the measurement instrument, preconcentration for trace analysis, matrix replacement, etc.), therefore, sample treatment is a must of the total analytical process. For this reason, López-Lorente et al. recently defined the 10 principles of Green Sample Preparation (GSP) [3]. The second and third principles of the 10 GSP principles call for the use of safer solvents and reagents, and for the use of sustainable, reusable and renewable materials. Therefore, Deep Eutectic Solvents (DESs) have recently emerged as one of the most promising alternatives to the employment of hazardous organic solvents. DESs, introduced by Abbot et al. in 2003 [4], are eutectic mixtures of two or more compounds that, because of interactions (i.e., hydrogen bonds and van der Walls forces) between their components, create a liquid eutectic mixture at temperatures lower than the melting points of the constituent compounds, being most of them nontoxic and eco-friendly extraction solvents. Additionally, natural deep eutectic solvents, often known as NADESs, are another sub-class of DES whose components are originated from nature [5]. NADESs possess the same physical and chemical properties than DESs as low or non-toxicity, low vapor pressure, high thermal stability, simplicity of synthesis at room temperature, high purity, and low cost. On the other hand, DESs and NADESs are also known as cheap analogues of ionic liquids.

Recently, an increased interest in the use of DESs and NADESs in microextraction processes has been experienced, in part because of their structural adaptability and broad applicability, and because of their hydrophilic/hydrophobic nature, which can be customized to suit the application. In addition, this family of emerging solvents is increasingly being used for novel analytical approaches more environmentally friendly than traditional methods, which are based on harmful organic solvents. But unfortunately, not everything is positive and there are always limitations. The Achilles heel of DESs and NADESs is their high viscosity and poor compatibility with instrumental analytical systems. This fact is responsible for the dilution of the extractant phase before analysis, in most cases, resulting in a loss of sensitivity. Therefore, a compromise needs to be found to develop methodologies that provide excellent metrics. All these aspects will be commented and comparatively discussed.

Acknowledgements

The authors are grateful to the Spanish Ministry of Science and Innovation (PID2021-126155OB-I00), the Regional Government of Valencia (Spain) (CIPROM/2021/062) and Instituto de Investigación Sanitaria y Biomédica de Alicante (ISABIAL, Alicante, Spain) (UGP-22-153) for the financial support. The authors extend their appreciation to Ministry of Science and Innovation for granting the Spanish Network of Excellence in Sample Preparation (RED2022-134079-T). This study is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society.

References

[1] A. Galuszka, Z. Migaszewski, J. Namieśnik, The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices. TrAC Trends in Anal. Chem. 50 (2013) 78-84.
[2] P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, Oxford, UK, 1998.
[3] A. López-Lorente, F. Pena-Pereira, S. Pedersen-Bjergaard, V.G. Zuin, S.A. Ozkan, E. Psillakis, The ten principles of green sample preparation. TrAC Trends in Anal. Chem.148 (2022) 116530.
[4] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Novel solvent properties of choline chloride/urea mixtures. Chem. Commun. (1) (2003) 70-71.
[5] Y.H. Choi, J. van Spronsen, Y. Dai, M. Verberne, F. Hollmann, I.W.C.E. Arends, et al., Are natural deep eutectic solvents the missing link in understanding cellular metabolism and physiology? Plant Physiol. 156(4) (2011) 1701–5.

Assessment of Analytical Systems by Metric Tools

KN-6

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Keywords: *Green analytical chemistry, Green sample preparation, Greenness assessment, Metric tools*

The search for fit-for-purpose analytical methods has been and continues to be one of the main aims of the field. In recent decades, this objective has been coupled with the need to improve analytical methodologies by minimizing or preferably avoiding their associated environmental, health and safety issues. In this sense, the introduction of the twelve principles of Green Chemistry [1] has been a particularly important milestone towards the development of greener processes focusing on a design-oriented approach. The subsequent introduction of principles more suited to the field, such as the twelve principles of Green Analytical Chemistry (GAC) [2] and, more recently, the ten principles of Green Sample Preparation (GSP) [3], have enabled significant improvements to be achieved in a more structured and defined way. These essential contributions set out aspects to be considered to achieve the greenest possible profile of analytical methods, while ensuring the required metrological aspects. In this regard, numerous analytical methods have been improved by minimizing chemicals and energy consumption, with a much reduced generation of wastes and less risk for the analyst without deteriorating the analytical characteristics, and even achieving significant improvements in terms of sensitivity and selectivity. In turn, the introduction of metric tools that can assist in the development and selection of greener methodologies is particularly desirable. Different metrics have been developed in recent years with the aim of facilitating the selection of more environmentally benign and safer alternatives to the harmful substances still used in a significant number of conventional methods. Metrics can also be very helpful to identify the limitations of analytical methods from the point of view of GAC and GSP and/or to compare (and select) different analytical systems according to their green profile.

The present contribution focuses on assessing the greenness profile of analytical systems. Selected examples involving tools that enable obtaining rankings of alternatives to facilitate the replacement of harmful substances by greener options are firstly described. Particular emphasis is then placed on the applicability and scope of application of metric tools with freely accessible software in line with the principles of GAC and GSP, namely the Analytical Greenness Calculator (AGREE) [4] and AGREEprep [5,6], respectively.

Acknowledgements

F. Pena-Pereira thanks the MCIN/ AEI / 10.13039/501100011033 / FEDER, UE (Project PID2022-136337OB-I00) for financial support.

References

[1] P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998.
[2] A. Gałuszka, Z. Migaszewski, J. Namieśnik, TrAC, Trends Anal. Chem. 50 (2013) 78-84.
[3] Á.I. López-Lorente, F. Pena-Pereira, S. Pedersen-Bjergaard, V.G. Zuin, S.A. Ozkan, E. Psillakis, TrAC - Trends Anal. Chem. 148 (2022) 116530.
[4] F. Pena-Pereira, W. Wojnowski, M. Tobiszewski, Anal. Chem. 92 (2020) 10076–10082.
[5] W. Wojnowski, M. Tobiszewski, F. Pena-Pereira, E. Psillakis, TrAC, Trends Anal. Chem. 149 (2022) 116553.
[6] F. Pena-Pereira, M. Tobiszewski, W. Wojnowski, E. Psillakis, Adv. Sample Prep. 3 (2022) 100025.

Research Progress in Solid Phase Microextraction

KN-7

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Keywords: *Adsorbent, Adsorption mechanism, Organic pollutant, Solid phase microextraction*

Recently, solid phase microextraction (SPME) has been coupled with the automatic sampler, making it more charming in the development of fast, efficient, and high-throughput methods. Moreover, the role of SPME on the investigation of structure-function relationship has been gradually explored, by coupling the SPME fiber with automatic sampler. It is important to elucidate the adsorption mechanisms of coating materials, which can provide new ideas for the synthesis of high-performance adsorbents, as well as the fabrication of multifunctional SPME coatings. A series of adsorbents have been prepared with precisely controlled microstructures, which can be ideal models to investigate the influence of functional group, pore structure and doping heteroatom on the adsorption performance. It has been found that the micropores can be effectively utilized by BTEX (benzene, toluene, ethylbenzene, and xylenes) with small molecular size, leading to ultra-high enrichment factors. As the molecular size increases, the target pollutants are inclined to be adsorbed on the surface of prepared adsorbents, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and musk. In particular, the functional groups and doping heteroatoms are potential to be effective adsorption sites, boosting the adsorption process via electrostatic interaction, hydrogen-bond interaction, hydrogen-π interaction and so on. The accessible F atoms in covalent organic framework (COF) have been confirmed to play important roles on the fast adsorption and effective extraction of per- and polyfluoroalkyl substances (PFAS) [1,2].

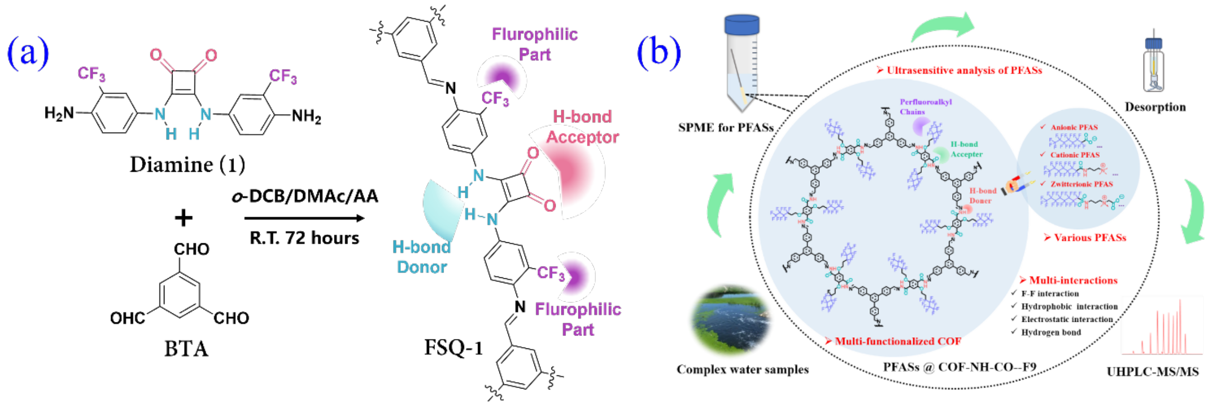

Figure 1. Facile synthesis of a fluorinated-squaramide COF (a) and multifunctionalized COF (b) for the effective extraction of PFAS.

References

[1] J. Huang, Y. Shi, G. Huang, S. Huang, J. Zheng, J. Xu, F. Zhu, G. Ouyang. Facile synthesis of a fluorinated-squaramide covalent organic framework for the highly efficient and broad-spectrum removal of per- and polyfluoroalkyl pollutants, Angew. Chem. Int. Ed. 2022, 61 (2022) e202206749.
[2] C. Song, J. Zheng, Q. Zhang, H. Yuan, A. Yu, W. Zhang, S. Zhang, G. Ouyang. Multifunctionalized covalent organic frameworks for broad-spectrum extraction and ultrasensitive analysis of per- and polyfluoroalkyl substances, Anal. Chem. 95 (2023) 7770-7778.

SPME for Trace Metal Speciation

KN-8

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Keywords: *SPME, Speciation, Mercury, Tin, Arsenic, Transition metals*

Total trace element content determination and speciation at the part-per-trillion level (ng L^{-1}) and part-per-quadrillion (pg L^{-1}) are challenging for most elemental detectors and become harder when complex samples are analyzed. Solid phase microextraction (SPME), in a single analytical step can provide analyte preconcentration along with matrix separation [1].

(Organo)metallic compounds can be collected by SPME from the sample headspace or liquid phase, directly or after derivatization. The usual separation method for the collected volatile species is gas chromatography. Non-volatile analyte species can be collected from the sample liquid phase and separated by liquid chromatography or capillary electrophoresis. Currently, most SPME applications in the inorganic field comprise aqueous phase alkylation of analyte followed by headspace extraction and gas chromatography separation combined with inductively coupled plasma mass spectrometry as detector of choice for ultra-trace detection of metals. The most studied metal species include tin, lead and mercury [2] species. The use of SPME for the study of equilibria in complex systems is also discussed and future roles of solid phase microextraction in the inorganic analytical field are raised

In recent years, a number of non-fiber based SPME approaches have been employed for inorganic analysis, including in-tube SPME, capillary microextraction, hollow fiber SPME, micropipette tip SPME, SPME on a stir bar, SPME on a microfluidic device and dispersive SPME. Additionally, the developments in dedicated SPME coatings for inorganic applications have been a burgeoning field of research enabling the microextraction of most transition metal ions, directly in solution, without the need for derivatization [3].

References

[1] Z. Mester, R Sturgeon, J. Pawliszyn Solid phase microextraction as a tool for trace element speciation, Spectrochimica Acta Part B 56 2001 233-260.
[2] Z. Mester, J. Lam, R Sturgeon, J. Pawliszyn, Determination of methylmercury by solid-phase microextraction inductively coupled plasma mass spectrometry: A new sample introduction method for volatile metal species, Journal of analytical atomic spectrometry 15 (2000) 837 – 842.
[3] E. Pagliano, Z. Mester, Solid Phase Microextraction for Trace Element Determination: The Fiber and Its Evolution, in: J. Pawliszyn (Ed.), Evolution of Solid Phase Microextraction Technology, RSC., London, 2023, pp. 95-134.

What 3D Printing Has to Offer in the Liquid Phase Microextraction Field

KN-9

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Keywords: *3D Printing, Liquid-phase microextraction, Milli/microfluidics*

Additive manufacturing has made tremendous strides in the sample preparation field over the last few years as demonstrated in a number of authoritative review articles [1-3]. Most of the efforts were however geared towards facilitating sorptive (micro)extraction procedures by exploiting the plethora of currently printable materials as sorptive phases. However, little interest seems to be focused on exploiting the distinct 3D printing technologies for aiding at the miniaturization and the high-throughput performance of liquid-phase microextraction (LPME) counterparts.

This keynote lecture will introduce the main assets of the various 3D printing technologies, such as fused deposition modelling, vat polymerization and photopolymer inkjet printing, for in-house manufacturing of supports, gaskets and functional platforms for expanding the applicability and fostering automation of distinct microextraction modalities, such as hollow-fiber supported LPME, single-drop LPME and in-syringe dispersive LPME. Particular focus is given in this lecture to recent developments in the field of electromembrane extraction (EME), in particular in a non-supported mode, by exploiting printable millifluidic devices obtained by vat polymerization of acrylate liquid resins with unrivalled geometry and unique surface energy of the inner walls as compared to glass, and fluorinated tubing that is demonstrated to ameliorate mass transfer whenever octanol is used as organic phase [4]. Recent research results in our group for miniaturization and automation of EME and improvement of enrichment factors by exploiting (i) programmable flow in a flow-injection arrangement, (ii) multiple-EME in the same printed device, and (iii) implementation of in-situ optosensing detection in the acceptor phase are presented and demonstrated by the determination of methylene blue as a charged species in troublesome matrices, such as textile dyeing wastewaters.

Acknowledgements

The authors acknowledge financial support from the Spanish State Research Agency (AEI), the Spanish Ministry of Science, Innovation and Universities (MICIU) and the European Union (NextGenerationEU/PRTR) through projects PID2020-117686RB-C33 (AEI//10.13039/501100011033/ MICIU) and TED2021-131303B-I00 (MICIU/AEI/ NextGenerationEU/PRTR). A.S. is grateful to the Government of the Balearic Islands for a postdoctoral scholarship (PD/003/2022). E.J.C.-C. also acknowledges the funding of the project PID2021-125459OB-I00 by the AEI/MICIU, the Advanced Materials Program supported by MICIU with funding from Next Generation EU (PRTR-C17.11) and by Generalitat Valenciana. The authors extend their appreciation to MICIU for granting the Spanish Network of Excellence on Sustainable sample preparation (RED2022-134079-T). This article is based on research from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society (DAC-EuChemS).

References

[1] D.J. Cocovi-Solberg, P.J. Worsfold, M. Miró, Opportunities for 3D printed millifluidic platforms incorporating on-line sample handling and separation, TrAC-Trends Anal. Chem. 108 (2018) 13-22.
[2] F. Li, M. Rodas-Ceballos, S.K. Balavandy, J. Fan, M.M. Khataei, Y. Yamini, F. Maya, J. Sep. Sci., 43 (2020) 1854-1866.
[3] Q. Zhu, C. Liu, S. Tang, W. Shen, H.K. Lee, Application of three dimensional-printed devices in extraction technologies, J. Chromatogr. A 1694 (2023) 463987.
[4] A. Sahragard, M. Dvorak, C. Pagan-Galbarro, E.J. Carrasco-Correa, P. Kuban, M. Miró, Anal. Chim. Acta 1297 (2024) 342362.

Extraction Strategies for Studies of Plant-Insect and Environmental Contaminant Interactions

KN-10

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Keywords: *Green extraction techniques, Metabolomics, NSAID, Plant-insect*

The biodiversity of Colombia, a tropical South American country, with access to two oceans, the Pacific and the Atlantic (Caribbean Sea), is immense, second only to Brazil. Of the more than 45 thousand species of higher plants, less than 10% have been studied phytochemically. The combination of various sample preparation techniques and instrumental analysis makes it possible to carry out bioprospecting and the study of the relationship between plants and their environment, particularly between plants and insects, as well as the interaction of plant species and emerging contaminants (non-steroidal anti-inflammatory drugs). The presentation will compare several extraction techniques (HS, P&T, HS-SPME, SFE, MSPD, and others) applied to the isolation of secondary metabolites from plants, according to their chemical nature (volatility, polarity), in combination with high-resolution analytical techniques (GCxGC/MS, UHPLC/LC, HRMS). Examples of application of analytical techniques to the study of flower fragrances, the interaction of insects with flowers and the transfer of secondary metabolites (xanthines, tropane and pyrrolizidine alkaloids) from plants to insects, as well as the absorption of emerging contaminants by some aquatic plants will be presented. A special emphasis will be placed on the application of in vivo techniques (HS-SPME) and green methods, which minimize the use of solvents (MSPD). A comprehensive use of plant material (aromatic plants) for distillation of essential oils and subsequent extraction of natural ingredients (flavonoids) from residual biomass will be matters of discussion. Unfortunately, there is no universal extraction method to isolate secondary metabolites from plants; it is necessary to resort to different techniques and analytical methods to create and expand the increasingly widespread database of natural substances, useful for the construction of the metabolomic map of tropical plant species.

Combining Microextraction and Mass Spectrometry Using (Bio)Polymer Sorptive Phases Hosted in Stainless Steel Needles

KN-11

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***Keywords:** Ambient ionization mass spectrometry, Biofluids, Electrospray, Needles, Sample preparation*

The ideal situation for the analysis of complex samples (e.g., biofluids, food, wastewater) implies the dilution and subsequent analysis by the so-called *dilute-and-shoot* modality. However, the sensitivity, selectivity, and compatibility of the sample with the instrumental technique, generally mass spectrometry (MS), is limited. Consequently, a sample preparation step is mandatory to preconcentrate the analytes, minimize or eliminate the interferences, and guarantee the compatibility of the sample extract with MS.

The main challenge of sample preparation is that it is a time-consuming process that requires a separation technique (chromatography, electrophoresis) prior to the MS analysis. Ambient ionization MS (AIMS) can overcome this limitation by substituting the separation technique with a previous sample clean-up step. Substrate spray MS (SSMS) is a modality of AIMS that uses sharped materials (paper, wooden tips, coated blades, aluminum foil, needles) to form the electrospray (ESI) containing the analytes when applying a high voltage and an organic solvent to elute and ionize the analytes that enter into the MS inlet.

Needles are affordable, disposable, and available materials that have been used in the design of novel interfaces by AIMS. Their hollow geometry allows the samples and solvents flow-through, while permitting the immobilization/host of sorptive phases. Consequently, they can act as ESI emitters and extraction devices. The first prototype consisted of the use of an inner-wall polydopamine-coated hypodermic needle (HN) [1] for the analysis of drugs of abuse in saliva. To enhance the sorptive phase-analytes interaction and speed-up the isolation step, a nylon-6/cotton composite was hosted into the Luer connection of the HN using methadone as the target compound [2].

However, the use of HNs presents some limitations: i) present finger pricking risk and ii) their geometry limits the amount of sorptive phase to be hosted. Therefore, blunt needles with a wider inner diameter were used to host a polydopamine/cotton composite for the determination of agonist-antagonist opioids in saliva. A pipette tip was used to reduce the inner diameter of the interface and allow the formation of the ESI [3]. Moreover, the pipette tip can host the sorptive phase instead of the needle. Strong cation-exchange pipette tips were used as sorptive phases for on-site and high-throughput analysis of urine samples containing codeine and morphine [4].

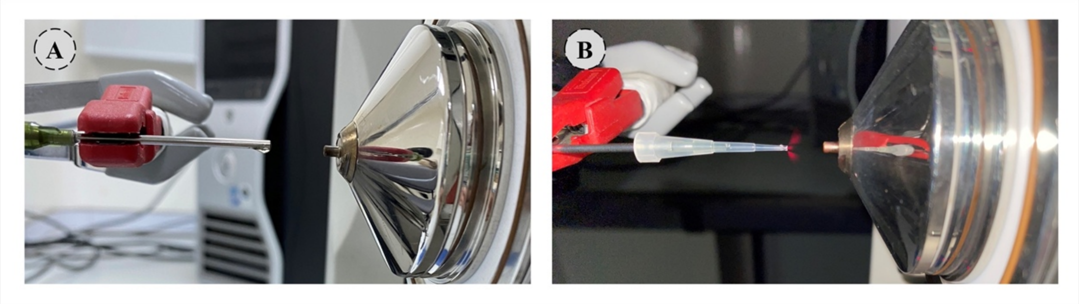

Figure 1. A) Lack of formation of the ESI using blunt needles and B) formation of the ESI using blunt needles attached to a pipette tip Reproduced from [3] under CC BY-NC-ND 4.0 license.

References

[1] C. Vejar-Vivar, J. Millán-Santiago, C. Mardones, R. Lucena, S. Cárdenas, Polydopamine inner wall-coated hypodermic needle as microextraction device and electrospray emitter for the direct analysis of illicit drugs in oral fluid by ambient mass spectrometry, Talanta, 249 (2022) 123693.

[2] J. Millán-Santiago, R. Lucena, S. Cárdenas, Nylon 6-cellulose composite hosted in a hypodermic needle: Biofluid extraction and analysis by ambient mass spectrometry in a single device, J. Pharm. Anal. 13 (2023) 1346–1352.

[3] J. Millán-Santiago, R. Lucena, S. Cárdenas, Bioinspired composite packed in blunt needles, integrated microextraction and determination of oxycodone and naloxone in saliva by substrate spray mass spectrometry, Anal. Chim. Acta. 1297 (2024) 342376.

[4] J. Millán-Santiago, R. Lucena, S. Cárdenas, Pipette tip-spray mass spectrometry for determining opioids in urine, from on-site micro-handling to high-throughput centrifugal microextraction, *submitted* to Advances in Sample Preparation.

New Bio-Based and Green Solvents at High Pressure: An Option to Improve the Sustainability of Sample Preparation Methods

KN-12

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Keywords: *Green Solvent, NADES, Supercritical Fluid Extraction, Agricultural By-Products*

During the last decades, chemical laboratories have focused their efforts on the development of analytical environmentally friendly alternatives based on the Green Analytical Chemistry Principles (GAC); being a key step in the whole analytical methodology, extraction has become one of the most important aspects to improve. In this sense, GAC should be employed in order to improve extraction processes related, for instance, to agricultural by-products by reducing potential environmental problems related to their extraction and revalorization, as suggested by the goal 12, "Sustainable consumption and production" of the 17 sustainable development goals (SDGs) set by the United Nations. Therefore, greener solvents and techniques are required in accordance with a sustainable procedure, reducing energy, reagents, and increasing the security of the applied analytical methodology. Natural deep eutectic solvents (NADESs), which are composed of major metabolites identified in plants and other organisms, could be green alternatives to extract bioactive compounds.

To achieve a greener process, the integration of green solvents with innovative and environmentally friendly technologies can offer some advantages such as time and energy reduction, as well as solvent consumption. In this sense, pressurized liquid extraction (PLE) and supercritical fluid extraction (SFE) have shown significant benefits for extracting bioactive compounds from natural matrices, despite being scarcely integrated with NADES as solvents.

In the present work, the solid residue from almond-based milk production has been employed in order to recover its fat content (rich in monounsaturated fatty acids and bioactive compounds such as α-tocopherol and vitamin A) by using a completely new approach consisting on the combination of supercritical CO2 extraction and a hydrophobic deep eutectic solvent (HDES) as a co-solvent. An HDES (eucalyptol-menthol of molar ratio 1:1) was chosen based on preliminary tests to be used as a co-solvent in supercritical extraction. The extractions were performed at 50 °C and 200 bar, employing a solvent flow of 4 mL/min. The HDES used as a co-solvent was employed at 0, 7.5, and 15%. Kinetic extractions were performed and the extraction was compared with the use of HDES under PLE conditions (using static and dynamic methods). Moreover, for the first time, the phase equilibrium of the selected HDES plus SC-CO2 was studied to determine the miscibility and phase behavior under the extraction conditions.

Results demonstrate that, under the selected conditions (15% HDES as a co-solvent, 50C and 200 bar), HDES was completely miscible with CO2 and the extraction took place under a single phase; the use of HDES accelerated the extraction of hydrophobic compounds from almond waste. Under these conditions, approximately 2.3 and 1.3 × more compounds were recovered compared to the conditions employing only CO2 and PLE in 30 min. Composition of almond extracts showed the presence of fatty acids: oleic, linolenic, palmitic, and stearic, and minor bioactive compounds such as α-tocopherol and campesterol.

Therefore, this work shows the enormous possibilities of NADES under pressurized conditions to improve the recovery of target bioactive compounds, improving the efficiency of the extraction method while reducing the processing time and the use of toxic organic solvents. On the other hand, it also emphasizes the need of acquiring a more in depth knowledge on the behavior of NADES together SC-CO2 in order to better understand the improved properties of these new type of solvents.

Acknowledgements

E.I. acknowledges the Ministry of Education of Spain for the Grant "Ayudas Movilidad Estancias Senior (Salvador Madariaga 2022; PRX22/00146); M.M.S. and M.A.R thank the Fundação de Amparo à Pesquisa do Estado de São Paulo – (grant numbers: 2023/05722-6, 2018/14582-5, 2019/13496-0).

Advances in Sample Preparation for the Analysis of Aromatic Amines as Biomarkers in Urine

KN-13

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Keywords: *Automation, Derivatization, LPME, Miniaturization, SPME*

Several Aromatic amines (AA) have been classified as human carcinogens, and besides occupational exposure, tobacco smoke is the most important source of human exposure. They are metabolized in the body and can ultimately be excreted in urine as metabolites or free AA. AA concentrations in urine are therefore of relevance as a marker for tobacco smoke and/or occupational exposure. Their analysis is still demanding because of the matrix complexity and large variety of AA present at low concentrations in urine. Some protocols utilize LC-MS based approaches but typically require extensive offline sample preparation. As an alternative analytical method GC-MS based approaches after derivatization have frequently been described in literature. We introduced many years ago a derivatization approach based on a Sandmeyer-type iodination rection that can be carried out directly in aqueous matrices. Despite being successfully applied in environmental analysis, the urine matrix required a more sophisticated sample preparation including hydrolysis of protein and/or DNA adducts, pH-dependent liquid phase extraction steps, derivatization and, finally, SPME enrichment of the iodinated derivatives. At best, all these steps can be carried out with small sample volumes in order to allow the analysis of valuable archived urine samples, e.g., from cohort studies.

The aim of our work was therefore to develop an automated analytical method for the trace analysis of AA in small urine sample volumes. In the presentation the focus will be on the automation procedures implemented for several steps using a xyz-based autosampler system [1] and the improvement of the miniaturized pH-dependent extraction step comparing Hollow fiber liquid phase microextraction (HF-LPME) and Parallel artificial liquid membrane extraction (PALME) [2], see figure 1. Furthermore, a comparison of MS detection modes for iodinated compounds will be shown [3] since selectivity and sensitivity in the MS detection step also influences the required sample preparation.

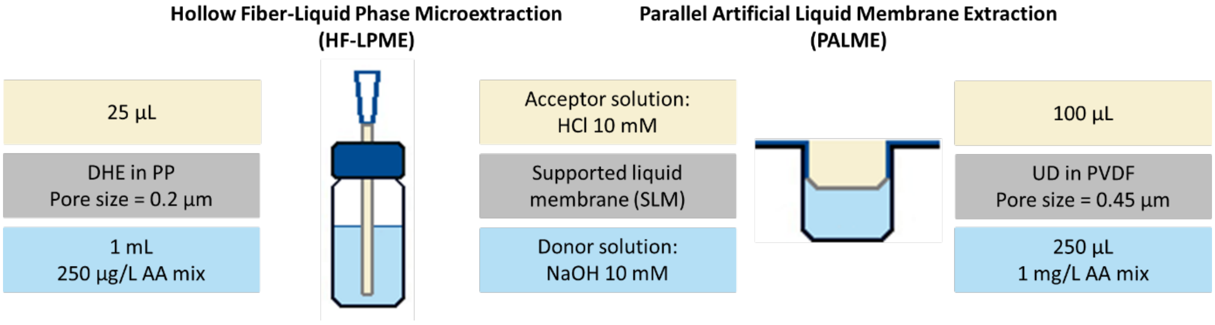

Figure 1. Schematic representation of the HF-LPME and PALME (one well) set-ups, including conditions finally chosen in this study.

Acknowledgements
We acknowledge financial funding of parts of this research by a PhD fellowship to NLP sponsored by Evonik Industries AG, Essen, Germany.

References

[1] N. Lorenzo-Parodi, W. Kaziur-Cegla, T. C. Schmidt, Automation and optimization of the sample preparation of aromatic amines for their analysis with GC-MS, Green Anal. Chem. 6 (2023), 100071.
[2] N. Lorenzo-Parodi, W. Kaziur-Cegla, A. Gjelstad, T. C. Schmidt, Liquid Phase Microextraction of Aromatic Amines – Hollow Fiber-Liquid Phase Microextraction and Parallel Artificial Liquid Membrane Extraction Comparison, Anal. Bioanal. Chem. 415 (2023), 1765-1776.
[3] N. Lorenzo-Parodi, E. Leitner, T. C. Schmidt, Comparison of gas chromatographic techniques for the analysis of iodinated derivatives of aromatic amines, Anal. Bioanal. Chem. 415 (2023), 3313–3325.

Miniaturizing the Already Miniaturized: New Ways to Achieve Dispersion of Magnetic Sorbents in the Analysis of Low-Volume Samples

KN-14

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Keywords: *Biomarkers, Dispersive, Magnetic, Microextraction, Miniaturization*

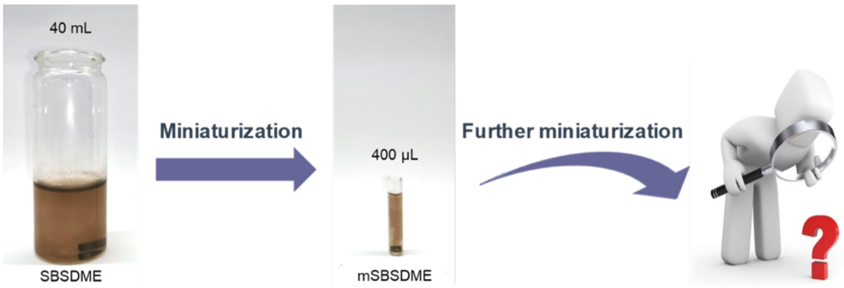
The determination of biomarkers in biological samples is usually challenging. The low levels of some of these biomarkers along with the high complexity of the matrices, makes their determination extremely difficult.

Conventional microextraction techniques have shown excellent performance for enriching and cleaning-up, and researchers in this field have known to evolve and adapt to the trends and needs of the moment, looking for safer and greener extraction phases and/or reducing their amounts. However, the efforts on reducing sample amount are still scarce, so these classical microextraction techniques are frequently limited when large volumes of sample are not available, as often occurs in biological fluids either due to the nature itself (*e.g.*, saliva, follicular fluid, cerebrospinal fluid, among others) or due to the person under study (*e.g.*, newborns or immunosuppressed patients). It should be added to this limitation that the need for having results as quickly as possible and also from a huge number of samples might collapse laboratories, which could be alleviated by using automated systems. Finally, it should not be obviated the biological risk that this type of samples presents, as well as the need to avoid cross-contamination in the treatment of successive samples. For this reason, it is more than recommendable to design sustainable single-use disposable extraction devices.

With the aim of contributing to the development of new microextraction approaches that satisfy all these demands, we have focused our attention on miniaturizing the already miniaturized, looking for approaches that allow a high-throughput, can be automated, and are affordable and compatible with low-volume samples by using affordable and disposable extraction devices.

Our starting point is the so-called stir bar sorptive dispersive microextraction (SBSDME) technique, developed by our research group ten years ago [1], which, unlike conventional dispersive solid-phase extraction (DSPE), integrates the dispersion and retrieval of the magnetic sorbent in a single device. This technique has been recently miniaturized (mSBSDME) to be applicable to low-volume samples by reducing the extraction device, which also allows to treat several samples simultaneously as a consequence of the reduction of the physical space thus providing a higher sample throughput [2].

Therefore, this keynote is focused on our recent achievements in this field, showing new approaches based on new ways to disperse magnetic sorbents in low-volume samples.



Acknowledgements

Grant PID2020-118924RB-I00 funded by Spanish Ministry of Science and Innovation (MCIN/AEI/10.13039/501100011033) is greatly appreciated. This contribution is based upon work from the National Thematic Network on Sample Treatment (RED2022-134079-T) of the Spanish Ministry of Science and Innovation, and the Sample Preparation Study Group and Network supported by the Division of Analytical Chemistry of the European Chemical Society.

References

[1] J.L. Benedé, A. Chisvert, D.L. Giokas, A. Salvador, Development of stir bar sorptive-dispersive microextraction mediated by magnetic nanoparticles and its analytical application to the determination of hydrophobic organic compounds in aqueous media, J. Chromatogr. A 1362 (2014) 25–33

[2] C. Azorín, J.L. Benedé, A. Chisvert, New challenges in sample preparation: miniaturized stir bar sorptive dispersive microextraction as a high-throughput and feasible approach for low-availability sample preparation, Anal. Chim. Acta 1238 (2023) 340627

Improved Analysis of Complex Samples Thanks to More Environmentally-Friendly and Selective Sample Preparation Methods

KN-15

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Keywords: *Immunosorbents, Miniaturization, Molecularly imprinted polymers, Oligosorbents, Solid-phase extraction*

The evolution of instrumentation in terms of separation and detection has enabled a real improvement in sensitivity and a reduction in analysis time. However, the analysis of trace or ultra-trace compounds from complex samples such as biological fluids often requires a purification and pre-concentration step prior to chromatographic analysis. Liquid-liquid extraction and solid-phase extraction are the most widely used pre-treatment techniques, and have been the subject of much work for the extraction of molecules of interest from liquid samples, or the purification of extracts from solid samples. However, despite their efficiency, both methods still suffer from the fact that they require a large quantity of solvent in relation to the sample size, especially in the case of liquid-liquid extraction. They also lack selectivity for the analysis of ultra-traces of targeted analytes in complex samples. Indeed, as the partitioning/extraction mechanism is mainly based on the polarity of the molecule, this leads to potential co-elution during subsequent chromatographic analysis, generating matrix effects during mass spectrometry quantification too, despite the specificity of this detector.

Solvent consumption can be reduced by miniaturizing the extraction device. In addition, the use of solvents that are more environmentally friendly than conventional organic solvents can also limit the impact of the method in terms of sustainability.

With regard to the lack of selectivity of extraction methods, carriers implementing a molecular recognition mechanism can be developed. These are powerful tools for the selective extraction of a target molecule and its structural analogues, enabling more reliable and sensitive quantitative analysis at trace level. For example, immunosorbents based on the use of antibodies specific to the molecule(s) of interest, oligosorbents based on the use of aptamers (i.e. sequence-specific oligonucleotides capable of binding a given molecule or ion with the same affinity as antibodies) and molecularly or ionically imprinted polymers, the synthesis of which leads to the formation of specific cavities mimicking the antibody recognition site, are three types of support that can improve the selectivity of the extraction procedure.

Indeed, these tools enable matrix components to be eliminated during sample processing, thus avoiding the risk of matrix effects widely encountered in LC/MS. Their miniaturization and on-line coupling with nanoLC also contribute significantly to reducing solvent consumption. Several applications on real samples will be presented to illustrate the enormous potential of these tools applied to complex samples of just 50-150 nL.

Green, Sustainable and Circular Separation Science

KN-16

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Keywords: *Miniaturization, Obstacles, Separation mode, Separation technique*

Chemistry as a scientific discipline has a significant contribution to the well-being of mankind. Chemistry helps us solve global problems related to food, energy, healthcare and materials needs. However, once such primary needs are met human ingenuity gets further tested to find even better solutions that require only minimal resources, yield maximal comfort and have a reduced impact on our environment. Sometimes these endeavors are not grounded in reality – good examples are alchemists' centuries-long efforts to convert common metals to gold, or early physicists' attempts to create a perpetuum mobile, in other words to create eternal movement without any energy consumption. Whenever such dreams clash with our dimension/space-reality, new laws emerge reminding us what is possible and what is not within the limits set by Mother Nature. In the last 2-3 decades we continuously talk about green, sustainable and circular chemistry, a major contemporary dream. As clearly debated in the scientific literature, the guiding principles of green, sustainable and circular chemistries are quite different [1] and we shall deal with each of them ideally separately, even if some of their global goals can be viewed as quite similar or at least somehow overlapping. If one takes some of the principles of green, sustainable and circular chemistry strictly one can easily arrive to the conclusion that the basic laws of the universe such as the first-, the second- and the laws of thermodynamics exclude the realization of some of the principles of the envisioned green, sustainable and especially of circular chemistry [2]. Nevertheless, if one approaches these principles with a free spirit, by considering the coupling of spontaneous and non-spontaneous processes, by harvesting and harnessing still undiscovered or unused sources of energy and materials, then staying within nature's strict principles seems more realistic.

In this presentation we will formulate our thoughts on, Green, Sustainable and Circular Separation Science, a field of Analytical Chemistry developed for the characterization of the chemical composition of matter. In all fields of science, we look first of all for new knowledge/information. One fundamental point what distinguishes Analytical Chemistry from several other branches of chemistry is that in Analytical Chemistry we rather look for new information than for novel materials. The fundamental laws of the universe such as the Law of Mass Conservation, the Laws of Thermodynamics, the Theory of Specific Relativity and the Principle of Mass–Energy Equivalence concern mass and energy and their interrelationship. Since 1961 a conversation has emerged on the physicality of information [3,4], its mass [5,6] that led to the proposed Principle of Mass-Energy-Information Equivalence [6]. However, many issues in this area are still under debate [7]. Independent of the answers to the abovementioned epistemology considerations, it is obvious that we cannot get information without any input of mass and energy. Therefore, the strategies of making separation science greener, sustainable and circular in our opinion are the following: 1) Critical selection of the separation method; 2) Selection of chemicals used (i.e. mobile phase components); 3) Recirculation of waste (of mobile phase); 4) Miniaturization; 5) Sensors (giving up separation altogether). In this presentation each of these approaches will be critically discussed and highlighted by examples from the author's own laboratory experience and from the relevant literature.

References

[1] H. Mutlu, L. Barner, Getting the Terms Right: Green, Sustainable, or Circular Chemistry? Macromol. Chem. Phys. 223 (2022) 2200111.
[2] K. Kümmerer, Sustainable Chemistry: A Future Guiding Principle, Angew. Chem. Int. Ed. 56 (2017) 16420–16421.
[3] R. Landauer, Irreversibility and heat generation in the computing process, IBM J. Res. Dev. 5 (1961) 183–191.
[4] R. Landauer, The physical nature of information, Phys. Lett. A 217 (1996) 188–193.
[5] L.B. Kish, C.G. Granqvist, Does Information Have Mass? Proceedings of the IEEE 101 (2013) 1895-1899.
[6] M.M. Vopson, The mass-energy-information equivalence principle, AIP Advances, 9 (2019) 095206.
[7] M. Burgin, R. Mikkilineni, Is Information Physical and Does It Have Mass? Information 13 (2022) 540.

7. Invited Presentations

Low Solvent Consumption Online Liquid-Gas Chromatography-Tandem Mass Spectrometry for Polycyclic Aromatic Hydrocarbon Determination in Olive Oil

INV-1

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Keywords: *Extra virgin olive oil, Green sample preparation, Liquid-gas chromatography, Polycyclic aromatic hydrocarbons, Tandem mass spectrometry.*

A dilute-and-inject liquid-gas chromatography-tandem mass spectrometry method is herein proposed, for the rapid determination of sixteen polycyclic aromatic hydrocarbons (PAHs) in extra-virgin olive oil (EVOO); sample preparation was very simple, inasmuch that it involved only a dilution step, thus avoiding extraction, clean-up and thus a high consumption of organic solvents. A side-by-side comparison of the selected-ion-monitoring and the pseudo multiple-reaction-monitoring (p-MRM) acquisition modes was performed, in terms of specificity and detectability. The results obtained using the p-MRM mode were superior and for this reason it was chosen as the acquisition mode. The method was linear over the concentration range 1-200 μg kg^{-1} (and 5-200 μg kg^{-1} in three cases). Accuracy (at the 2 μg kg^{-1} and 20 μg kg^{-1} concentration levels) was in the 86.9-109.6% range, with an RSD < 10%. Intra-day and inter-day precision (at 2 μg kg^{-1} and 20 μg kg^{-1} concentration levels) were in the 1.2-8.8% and 3.2-10.8% range, respectively. For all the PAHs, a negative matrix effect was observed. Three ouf of sixteen PAHs were detected in three EVOOs (among ten samples), albeit at the low ppb level.

Acknowledgements
The authors thank Shimadzu Corporation and Merck Life Science for their continuous support.
Funding: This research was supported by the Ministry University and Research within project PRIN 2022 PNRR titled “gReen analytical methods for PAHs detection in EVOO: from lABoratory to smart LabEl (RELIABLE)”, Prot. P2022842MJ, CUP J53D23014520001.

The Complex World of Eutectic Solvents and Their Use in Sample Preparation

INV-2

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***Keywords:** Eutectic solvents, Green analytical chemistry, Liquid-phase microextractions, Sample preparation*

Low transition temperature mixtures were already known in the 50s of the twentieth century. In 2003, Abbott and his co-workers, studying mixtures of choline chloride with urea and carboxylic acids that were liquid at ambient temperature, coined the term "deep eutectic solvent" (DES), i.e., any mixture whose melting point is deeply lower than those of the pure starting components [1]. In 2014, Abbott and his group expanded the definition of DES as eutectic mixtures of Lewis or Brønsted acids and bases which can contain a variety of anionic and/or cationic species [2]. In 2019, Coutinho and his co-workers refined the concept: DES are mixtures for which the eutectic temperature is far below that of an ideal liquid mixture (eutectic solvent, ES) and a so-called liquid window (the composition range at which they are in the liquid state) must be considered instead of a precise composition [3].
The term DES is now normally used in Analytical Chemistry, but many authors often do not go into a detailed characterization of the prepared mixtures to clear their real nature. Instead, they logically focus mainly on the analytical part, emphasizing the advantages that the liquid mixture provides. Therefore, it may happen that the solvent used is designated as a DES, but actually it is something different and, especially when it is used for sample preparation purposes, this rough identification can complicate understanding the actual role of the mixture in the extraction process. This communication presents some illustrative examples of eutectic solvents [4] and low transition temperature mixtures (LTTM) [5,6], their characterization and applications trying to highlight peculiarities, advantages, and limitations within the field of sample preparation.

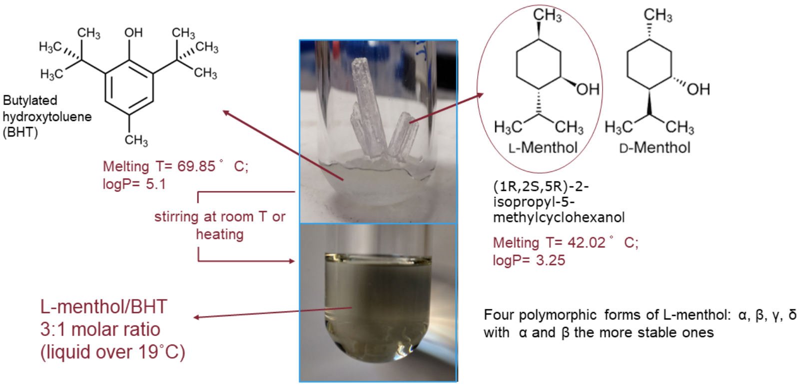

Figure 1. Preparation of an eutectic solvent (L-menthol:BHT, 3:1 molar ratio) with antioxidant properties.

References

[1] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Novel solvent properties of choline chloride/urea mixtures, Chem. Commun. 1 (2003) 70-71.
[2] E. L. Smith, A. P. Abbott, K. S. Ryder, Deep eutectic solvents (DESs) and their applications, Chem. Rev. 114 (2014) 11060-11082.
[3] M.A.R. Martins, S.P. Pinho, J.A.P. Coutinho, Insights into the nature of eutectic and deep eutectic mixtures, J. Solution Chem. 48(2019) 962–982.
[4] C. Dal Bosco, V. Di Lisio, P. D'Angelo, A. Gentili, Hydrophobic eutectic solvent with antioxidant properties: application for the dispersive liquid–liquid microextraction of fat-soluble micronutrients from fruit juices, ACS Sustainable Chem. Eng. 9 (2021) 8170-8178.
[5] P. Tomai, P. D'Angelo, I. Persson, A. Martinelli, V. Di Lisio, R. Curini, C. Fanali, A. Gentili, A low transition temperature mixture for the dispersive liquid-liquid microextraction of pesticides from surface waters, J. Chromatogr. A. (2019) 360329.

Blueness: Criterion in Chemical Analysis

INV-3

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Keywords: *Applicability, BAGI****,*** *Blueness, Greenness, Practicality*

Since green chemistry has dynamically entered first in chemistry science and later on in Analytical Chemistry, it actually predonimated over time and now has become the cornerstone in every analytical method' s development and use.[1]
The vast majority of methods have been revised in the aspect of their greenness. Many metric tools have been developed to evaluate the green character of the analysis.
But is greenness the only criterion we have to take into consideration upon selection of a method?
Important though it is, greenness can't be the only factor that an analytical scientist must evaluate when choosing the appropriate method (including sample preparation) [2].
Of course, protecting the environment and ensuring the operator's safety should be top priorities, but we should also consider, the practicality, in terms of several parameters including the type of analysis, the number of compounds that can be determined in one run, the analytical technique and required instrumentation, the throughput, the commercial availability of reagents, the automation degree, the need of pre-concentration to meet legislation criteria etc.
Additionally, an important aspect is the possibility to deviate from the protocol (especially important for accredited laboratories) and its adaptability.
These questions – and probably more– demonstrate the need to evaluate more parameters rather than only greenness as the single important factor when we evaluate a proposed method or protocol. The applicability and practicality of the method are of equal importance. Therefore, it is time to reconsider method selection so that all relevant factors are taken into consideration. In this aspect, the Blue Applicability Grade Index (BAGI) has been proposed to identify the weak and strong points of the method. The software is free and available at: bagi-index.anvil.app, generating an asteroid pictogram that designates the applicability and functionality of the analytical method and provides a final score on a scale of 25 to 100 **(Figure 1)**. The color "blue" is inspired by the red-green-blue (RGB) model –encompassing the "White Analytical Chemistry" concept and a score higher than 60 proves that the method under evaluation is practical and can be readily adopted. [3,4]
BAGI has already attracted the attention of analytical scientists and is used in the evaluation of newly developed methods. Blueness can be assessed by BAGI as a complementary tool along with available greenness metric tools in the hands of scientists in the chemical community.

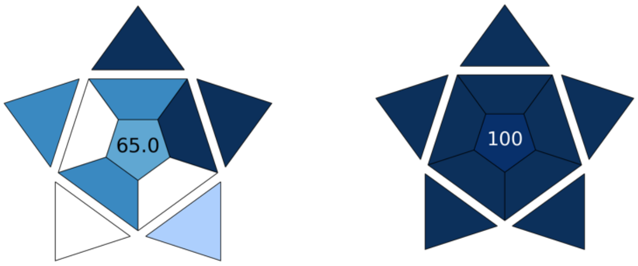

Figure 1. BAGI pictograms. Left: Practical method and Right: ideal method.

Acknowledgements
The author wishes to thank the co-authors of the original work: Natalia Manousi, Wojciech Wojnowski, and Justyna Płotka-Wasylka, for the co-operation in the software preparation.

References
[1] P. T. Anastas, Crit. Rev. Anal. Chem. 29 (1999) 167–175.
[2] Á. I. López-Lorente, F. Pena-Pereira, S. Pedersen-Bjergaard, V. G. Zuin, S. A. Ozkan and E. Psillakis, TrAC - Trends Anal. Chem. 148 (2022) 116530.
[3] P. M. Nowak, R. Wietecha-Posłuszny, J. Pawliszyn, Trends Anal. Chem. 138 (2021) 116223.
[4] N. Manousi, W. Wojnowski, J. Płotka-Wasylka, V. Samanidou, Green Chem. 25 (2023) 7598-7604.

Potential of Deep Eutectic Solvents in the Extraction of Pesticides from Plant Foods

INV-4

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Keywords: *Food, Liquid chromatography, Mass spectrometry, Matrix solid-phase dispersion extraction, Pesticides*

Pesticides are synthetic chemical compounds extensively used in agriculture. Due to direct exposure, bioaccumulation, and biomagnification, pesticide residues can pose health risks such as an increased risk of cancer, reproductive toxicity, neurotoxicity, immunotoxicity, and cytotoxicity. Therefore, it is crucial to identify and monitor these contaminants using appropriate analytical methods. The analysis of pesticides in foods requires sample pretreatment before their determination through analytical instruments. Commonly employed Liquid-Liquid Extraction (LLE) and Solid-Phase Extraction (SPE) methods require a significant amount of extraction time and toxic organic solvents [1].

In 2015, the United Nations introduced a sustainability-focused development plan called "Transforming Our World: The 2030 Agenda for Sustainable Development." This plan emphasizes the urgency of addressing pollution and toxicity in chemical processes, particularly focusing on reducing organic solvents and chemical waste in the environment. Deep eutectic solvents (DESs) and natural deep eutectic solvents (NADESs) have emerged as crucial components in sustainable chemistry, providing alternatives to traditional organic solvents in synthesis, extraction, and compound separation [2].

The most commonly used methods to enhance extraction processes sustainably in analytical chemistry and align with the key principles of green chemistry involve downsizing extraction by using minimal sample and solvent volumes, along with the potential substitution of organic solvents with eco-friendly alternatives like DES. DESs are known for being non-toxic, cost-effective, easy to prepare, and environmentally friendly, exhibiting qualities such as biodegradability and biocompatibility. They have been applied in analytical sample preparation, enabling the development of various microextraction methods that enhance the eco-friendly characteristics of the overall analytical process. Typically comprised of a hydrogen-bond acceptor and donor, DESs have lower melting points than their individual components.

Research has shown that DESs are effective in extracting a wide range of molecules compared to conventional organic solvents, resulting in high extraction yields. Their applicability to food sample preparation, whether hydrophilic or hydrophobic, requires the selection of DESs based on the chemical and physical properties of the analytes to achieve optimal extraction efficiency. DESs have been employed in the extraction and analysis of pesticides in food samples [1].

We have developed and validated various analytical methods utilizing techniques for extracting pesticides from food matrices, such as Matrix Solid-Phase Dispersion using DESs. Innovations involving the use of DESs not only as extractive solvents but also as extraction enhancers with dispersive materials have been tested.

These developed applications of DESs in sample preparation for extracting and analyzing pesticides in food products, such as hazelnuts and tomatoes, will be presented.

Acknowledgements

INAIL project “Tecniche di analisi innovative e approccio “omico” per l'analisi di esposizione a fitofarmaci”, Bando Ricerche in Collaborazione (BRiC-2022), CUP C83C2200147000.

References

[1] C. Hu, J. Feng, Y. Cao, L. Chen, Y. Li. Deep eutectic solvents in sample preparation and determination methods of pesticides: Recent advances and future prospects. Talanta 266 (2024) 125092.

[2] J. Liu, X. Li and Kyung Ho Row. Development of deep eutectic solvents for sustainable chemistry. Journal of Molecular Liquids 362 (2022) 119654.W. Strunk Jr., E.B. White, The Elements of Style, fourth ed., Longman, New York, 2000.

From "Green" to "Sustainable" Sample Preparation in the Analysis of Natural Products: Opportunities from New Materials Combined with Microextraction Techniques

INV-5

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Keywords: *Green phases, Metabolomic, Method assessment, Microextraction, Natural products*

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

Most studies and official methods for these matrices still use traditional extraction techniques, which have a significant impact on the environment. However, the development of new and more environmentally friendly alternatives that are more in line with the principles of Green Analytical Chemistry has progressively increased in recent years. Strategies include the use of miniaturized techniques and new classes of more environmentally friendly extraction phases [1]. However, it is also important to remember that accurate and reliable measurements are required, especially for industrial quality control laboratories that have to deal with a variety of norms and quality standards to ensure safe products for the public, and that practical considerations such as productivity, cost and simplicity of methods should not be neglected [2]. This contribution explores the possibility of improving the environmental footprint of sample preparation while maintaining adequate analytical performance and laboratory productivity. This is done through a series of case studies dealing with the extraction of chemically diverse, specialized metabolites from natural products. A particular focus is on the use of renewable and tailorable materials in combination with technologies that enables to increase extraction kinetics, such as microwave-assisted extraction. In addition, the proposed methods are evaluated in terms of their overall performance using appropriate metric tools. The aim is to move towards "sustainable" analytical methods, where the improvement in terms of environmental impact is assessed together with productivity (which influences the economic aspect) and analytical performance, which should ensure high quality health products for all.

References

[1] G. Mastellone, A. Marengo, B. Sgorbini, P. Rubiolo, C. Cagliero, New phases for analytical scale extraction from plants: Current and future trends. TrAC Trends Anal. Chem. 141 (2021) 116288

[2] G. Bechis, B. Raccary, E. Sarrazin, E. Corbi, C. Peres, N. David, C. Bicchi, C. Cagliero, Assessing the environmental and overall performance of gas chromatographic analyses. Development of a comprehensive evaluation framework and application to routine chiral analyses of fragrances as a case study. Sustain. Chem. Pharm. 35 (2023) 101217

Sample Preparation and GC×GC : Fundamental Alleys to Unravel MOSH and MOAH Contamination

INV-6

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Keywords: *GC×GC, Mineral oil hydrocarbon*

Food analysis is swiftly evolving, embracing advanced analytical techniques to tackle increasingly complex inquiries. In the realm of analytical chemistry, two overarching trends are discernible. On one front, sample preparation methodologies are gravitating towards more efficient, compact, and potentially solvent-free approaches. Conversely, in instrumental development, there's a preference for robust techniques to maximize data yield per analysis. Achieving this objective necessitates enhancements in both chromatographic separation and detector systems. In this context, the introduction of comprehensive 2D GC (GC×GC) by Phillips in 1991 stands out as a remarkably versatile and promising technique for food analysis. Presently, GC×GC has matured into a robust technique, although still facing resistance for its applicability for routine food quality, authenticity, and safety assessments. Its strengths lie in its capacity for simultaneous targeted and untargeted sample profiling, yet the synergistic role of sample preparation with GC×GC is often underappreciated. Effective sample preparation can significantly enhance GC×GC performance, thereby unlocking richer data insights. In exchange, the enhanced resolution achieved through GC×GC can simplify the sample preparation process, minimizing manipulation, solvent consumption, and time.

In this presentation, we will delve into the mutually beneficial relationship between GC×GC and sample preparation methods, particularly in the field of mineral oil hydrocarbon (MOH) contamination in food. The development and validation of a fully integrated LC-GC×GC-TOFMS/FID system [1] is discussed, as well as the ratio during the LC purification and before the chromatographic process to significantly improve the reliability of the data generated and mitigate the uncertainties in the analytical workflow. Particular focus is given to the optimization of an alternative chromatographic purification to the time-consuming, less reliable, and error-prone epoxidation procedure used for MOAH purification. Notably, it achieves a much lower quantification bias, around 5%, compared to over 40% with epoxidation. At the same time the improvement of the routine the extraction of MOH from edible oil through the employment of a microwave-assisted saponification method and a more suitable selection of the solvent mixture used for the saponification is discussed in light of the reduction of the overall uncertainty [2].

Acknowledgements
The authors want to thank Leco, Restek, and Milestone for their support

References

[1] Bauwens, G., Barp, L., & Purcaro, G. 2023. Validation of the liquid chromatography-comprehensive multidimensional gas chromatography-time-of-flight mass spectrometer/flame ionization detector platform for mineral oil analysis exploiting interlaboratory comparison data. Green Analytical Chemistry, 4, 100047. doi:10.1016/j.greeac.2022.100047.
[2] Bauwens, G., & Purcaro, G. 2024. Improved microwave-assisted saponification to reduce the variability of MOAH determination in edible oils, Analytical Chimica Acta, submit for publication.

Unconventional Solvents in Sample Preparation – Challenges Between Green and White Analytical Chemistry

INV-7

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Keywords: *Deep eutectic solvents (DESs), Green solvents, Ionic liquids (ILs)*

Green chemistry (GC) is nowadays highly recognised and considered as a holistic concept and exact science for a sustainable future. Considering the twelve GC principles [1], it must be emphasised that only some of them can be directly applied to analytical chemistry. The 12 principles of green analytical chemistry (GAC) were proposed a decade ago [2]. In fact, several GC and GAC rules are directly realted to green solvents. The development of new generations of environmentally friendly solvents is one of the most active area of research in green analytical chemistry.

According to current knowledge, the complete elimination of solvents, as the greenest choice in analytical procedures, is almost impossible. Therefore, eliminating hazardous solvents or replacing them with safer alternatives is a good way forward. If we need an ideal solvent with good dissolution properties, selectivity and extraction efficiency, it should definitely fulfil the following requirements: low toxicity, biodegradable, reusable, easy to obtain from renewable sources, low environmental impact and low cost. From an analytical point of view, the main challenge in the future will be to find a compromise between the increasing demands on the quality of the results (accuracy, LOD, reproducibility,...) and the whiteness of the method as well as the improvement of environmental friendliness [3]. In this presentation, two classes of unconventional solvents, ionic liquids (ILs) and deep eutectic solvents (DES) will be discussed with their basic chemistry and applications in food (natural products) and environmental analysis [4].

Acknowledgements
This work was supported by the Ministry of Education, Science and Technological Development of Serbia (contract number: 451–03-68/2022–14/200161).

References

[1] P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, Oxford, 1998.
[2] A. Gałuszka, Z. Migaszewski, J. Namieśnik, The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices, Trac. Trends Anal. Chem. 50 (2013) 78-84.
[3] P.M. Nowak, R. Wietecha-Posłuszny, J. Pawliszyn, White Analytical Chemistry: An approach to reconcile the principles of Green Analytical Chemistry and functionality, Trends Anal. Chem. 138 (2021) 116223.
[4] S. Ražić, J. Arsenijević, S. Đogo Mračević, T. Trtić-Petrović, Greener chemistry in analytical sciences: from green solvents to applications in complex matrices. Current challenges and future perspectives: a critical review, Analyst 148 (2023) 3130.

New Developments in Bioanalytical Applications of Solid Phase Microextraction

INV-8

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Keywords: *Bioanalytical applications, Metabolomics, Sample preparation, SPME*

Investigating roles, mechanisms, and the effect of triggers on biological systems are among the most important research lines that attract scientists from diverse disciplines. In this line of research, although in vivo investigation would provide more insightful knowledge about the system, only several methods are applicable for in vivo monitoring of metabolic changes in the biological systems. Moreover, in vivo assessment of the changes in metabolite levels can be also affected by the chosen sampling technique. For this reason, when working with biological systems, choosing the most appropriate sample treatment method to obtain a reliable data is of great importance.

Solid phase microextraction (SPME), a sample preparation method that can integrate the sampling and sample preparation in a single step, is one of the most important techniques applicable to in vivo and low/non-depletive sampling. The sampling principle of this technique depends on the equilibrium established between the free concentration of the analyte in the matrix and the extraction phase [1]. Alternatively, pre-equilibrium sampling based on mass transfer kinetics through the boundary layer surrounding the extractive phase can be used to extract from dynamic systems. Based on the sampling approach, various calibration strategies were developed to enable the determination of both total and free concentrations of a given analyte without any biospecimen removal from the system under investigation. Besides, when the extraction is performed with non-depletive samplers, the integrity of the physiological equilibrium of the studied system is preserved. Furthermore, SPME can take different shapes based on the demands of the study, and up to date, it has been prepared in fiber, arrow, micro tip, coated blade, coated mesh, flexible self supported thin films, or thin films on a support, and it has been utilized for numerous applications where standard approaches cannot be used [2].

In this presentation, SPME will be in the spotlight, and its power for untargeted and targeted metabolomics investigation in various bioanalytical applications, including in vivo investigations and clinical diagnostic studies will be discussed. In addition, novel extractive phases, samplers and instrumental coupling strategies will be discussed to give the perspective for new developments.

Acknowledgements

Presented studies were supported by Scientific and Technological Research Council of Turkey (TUBITAK) under the Grant Number 118Z435, 119Z863 and 120N352. The authors thank to TUBITAK for their supports.

References

[1] J. Pawliszyn, Handbook of Solid Phase Microextraction, Elsevier, 2011.

[2] N. Reyes-Garcés, E. Gionfriddo, G.A. Gómez-Rios, Md.N. Alam, E. Boyaci, B. Bojko, V. Singh, J.J. Grandy, J. Pawliszyn, Advances in solid phase microextraction and perspective on future directions, Anal. Chem. 90 (2017) 302-360.

8. Oral Presentations

Advanced Sample Preparation Using 3D Printing: From Conventional to Biomimetic Solid-Phase Extraction

O-1

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Keywords: *3D printing, Bioavailability, Biomimetic extraction, Novel designs, Solid-phase extraction*

3D printing is revolutionizing the world, offering new alternatives to old processes and novel applications that would have never been possible without this technology. Within this additive manufacturing mode, various technologies such as fused deposition modeling (FDM), vat polymerization, photopolymer inkjet printing, and selective laser sintering can be found, each with its own advantages and weaknesses. These 3D printing technologies enable the fabrication of novel structures that are difficult or costly to create using other methods, making 3D printing an intriguing alternative to consider. In Analytical Chemistry, the field of sample preparation has also embraced the benefits of 3D printing. These technologies offer new avenues for researchers to improve conventional methodologies like solid-phase extraction (SPE) [1], which is crucial for determining trace concentrations of analytes in different matrices. However, SPE sometimes falls short and additional information is needed. In this context, bioaccessibility and/or bioavailability of compounds in living organisms are an important parameter to study, but typically requiring *in-vivo* methodologies or tedious separation techniques [2]. Hence, recent innovative methodologies such as biomimetic solid-phase extraction (BMSPE) [3], when combined with 3D printing, can overcome the limitations of current methods and promote their widespread adoption in scientific research. This communication will discuss current trends in 3D printing for the development of novel devices in sample preparation, including SPE and BMSPE. It will also explore the characteristics of 3D printing technology that facilitate overcoming challenges in sample preparation and biomimetic studies. Additionally, the Green Chemistry perspective of 3D printing will be described. Relevant examples from CLECEM and FI-TRACE groups, showcasing the wide-ranging possibilities of 3D printing in sample preparation and biomimetic studies, will be selected to illustrate these points.

Acknowledgements

The authors acknowledge financial support from the Spanish State Research Agency (AEI//10.13039/501100011033/), the Spanish Ministry of Science, Innovation and Universities (MICIU) and the European Union (NextGenerationEU/PRTR) through projects PID2021-125459OB-I00, PID2020-117686RB-C33 and TED2021-131303B-I00. Also, the authors acknowledge the projects CIGE/2023/069, CIAICO/2022/183, INVEST/2022/107 and INVEST/2022/425 funded by Generalitat Valenciana. The authors extend their appreciation to MICINN for granting the Spanish Network of Excellence in Sample preparation (RED2022-134079-T). This communication is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society. This study forms part of the Advanced Materials programme and was supported by MCIN with funding from European Union NextGenerationEU (PRTR-C17.I1) and by Generalitat Valenciana.

References

[1] F. Li, M.R. Ceballos, S.K. Balavandy, J. Fan, M.M. Khataei, Y. Yamini, F. Maya, 3D printing in analytical sample preparation, J. Sep. Sci. 43 (2020) 1854-1866.

[2] E.J. Carrasco-Correa, J. Ruiz-Allica, J.F. Rodriguez-Fernandez, M. Miró, Human artificial membranes in (bio) analytical science: Potential for in vitro prediction of intestinal absorption-A review, TrAC Trends Anal. Chem., 145 (2021) 116446.

[3] M.P. Garcia-Moll, L. Garcia-Moll, E.J. Carrasco-Correa, M. Oliver, E.F. Simó-Alfonso, M. Miró, Biomimetic dispersive solid-phase microextraction: A novel concept for high-throughput estimation of human oral absorption of organic compounds, Anal. Chem., 95 (2023) 13123-13131.

Extraction of Emerging Contaminants from Treated Wastewater by a Polymeric Biodegradable Film and Following Analysis by Target and Non-Target LC-MS

O-2

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Keywords: *Design of experiments, Fabric phase sorptive extraction, Wastewater, White analytical chemistry*

The detection of known and unknown emerging contaminants (ECs) in wastewater is currently the object of numerous studies. Usually, especially if the target is a large set of analytes or if non-targeted approaches are selected, classical sample treatment strategies, such as solid phase extraction, are employed [1]. Still, the growing interest in green chemistry generates the need for the implementation of more sustainable innovative techniques. In the case of environmental contaminants, the use of sophisticated instrumentation such as LC-MS/MS - in low or high resolution - is mandatory, to guarantee optimal method performances for target studies and enhance the possibility of identifying unknown species in non-targeted ones. Nowak et al recently introduced the concept of “White analytical chemistry” [2] (WAC), which perfectly represents the requirements of environmental analysis, where greenness should always be combined with feasibility (time and cost-effectiveness) and satisfactory accuracy, precision and specificity.

In this framework, green sample preparation plays a pivotal role, and the use of novel versatile materials is desirable.

The present study deals with the application of a commercial patented biopolymer (Mater-Bi) to extract emerging contaminants from water samples. Its use was optimized for several analytes and then applied for the detection of contaminants by both target and non-target analysis by LC-MS/MS. The multivariate approach was followed for the optimization of the sample preparation, which finally resembled a fabric phase sorptive extraction method.

First, the interaction among 39 ECs with varying chemico-physical properties and the Mater-Bi film was investigated by two sequential experimental designs [3], to simultaneously study several factors and optimize extraction efficiency. The results indicated that hydrophobic and weakly acidic analytes were the most prone to interact with the material, resulting in good recovery from water samples. The final method, suitable for the determination of sixteen analytes (including pharmaceuticals, UV-filters, estrogens, BPA and triclosan), involved pH and ionic strength modification of the sample, 1 h extraction and desorption in ethanol.

This target method showed satisfactory recoveries from real wastewater (56-116%), as well as excellent precision (inter-day relative standard deviations below 10% for most compounds). Also, matrix effect was completely acceptable, allowing external calibration, and low limits of detection in matrix were achieved, from 0.004 to 0.159 µg L^{-1}, comparable to those from recent studies employing green extraction procedures. Moreover, it demonstrated superiority to classical methods, also in terms of feasibility and costs, according to the evaluation by the AGREE and Red Green Blue (RGB) metrics.

The method was applied to samples from an Italian wastewater treatment plant, which were analysed in both targeted and non-targeted modalities. Among the target chemicals, pharmaceuticals and UV filters were quantified, at the µg L^{-1} and ng L^{-1} levels, respectively. Due to the previous findings, it can be hypothesized that other contaminants with hydrophobic characteristics may be extracted by the film from the water samples. Thus, an LC-High Resolution MS method was implemented, using data independent analysis (DIA) by means of a Quadrupole-Time of Flight mass spectrometer, in both negative and positive mode. This strategy allows to fragment all ions coming from the quadrupole, independently from the intensity of their signal, thus increasing the possibility to tentatively identify contaminants at low concentrations. The main drawback is that the ions are all fragmented together, and assigning products to precursor ions is rather challenging. For this reason, data were analysed by the Region Of Interest- Multivariate Curve Resolution (ROI-MCR) chemometric method, which allows to extract the ions m/z values (based on specific thresholds) and then separate the contribution of different chemicals (components) based on the chromatographic profile. By applying this powerful chemometric workflow, the identification of unknown contaminants was attempted.

The developed method allowed a green, simple and extremely cheap extraction of ECs from treated wastewater, by using a material so-far unexplored in analytical chemistry. Moreover, it paves the way for the implementation of greener sample treatments in the field of non-target LC-HRMS analysis.

Acknowledgements
The authors acknowledge the European Union for funding this work, through the NextGeneration EU project “AWARE”.

References

[1] M. Paszkiewicz, K. Godlewska, H. Lis, M. Caban, A. Białk-Bielińska, P. Stepnowski, Advances in Suspect Screening and Non-Target Analysis of Polar Emerging Contaminants in the Environmental Monitoring. Trends in Analytical Chemistry, 154 (2022) 116671.

[2] P.M. Nowak, R. Wietecha-Posłuszny, J. Pawliszyn, White Analytical Chemistry: An Approach to Reconcile the Principles of Green Analytical Chemistry and Functionality, Trends in Analytical Chemistry, 138 (2021) 116223.

[3] B. Benedetti, V. Caponigro, F. Ardini, Experimental Design Step by Step: A Practical Guide for Beginners, Critical Reviews in Analytical Chemistry 52 (2022) 1015-1028.

Functionalized Membranes for Unveiling Metal Interactions with Microplastics and Organic Pollutants in Aquatic Systems

O-3

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Keywords: *Antibiotics, Divalent metal ions, Functionalized membranes, Microplastics, Natural water*

Increasing metal pollution in water is a critical issue that affects human health and the entire ecosystem. Metal pollutants are persistent environmental contaminants due to their resistance to degradation. Free metal ions exhibit the highest potential for bioaccumulation and toxicity compared to other forms of metal species within aquatic environments. Moreover, the interactions between free metal ions and other co-existing aquatic pollutants should not be underestimated. Metallic ions either can bond with pollutants, acting as ligands, or be adsorbed by other substances in the water, affecting the overall toxicity of the pollutant mixture.

Pharmaceutical compounds are becoming more commonly found in aquatic environments, such as antibiotics used to treat infectious diseases in both humans and animals. Sulphonamides, in particular, have been detected in aquatic ecosystems due to their non-biodegradable nature and strong hydrophilic properties. Sulfamethoxazole (SMX), the most commonly used sulphonamide in human medicine, and sulfamethazine (SMZ), a key sulphonamide in veterinary medicine, are among the prominent representatives of this group.

Recently, microplastics (MPs) have gained significant attention as pollutants due to their widespread presence in waters and soils worldwide. In addition to posing a direct concern, MPs are also troubling because they serve as ideal sites for the adsorption of other pollutants, including heavy metals and antibiotics. This is primarily due to their high hydrophobicity, expansive specific surface area, and resistance to degradation in the environment.

Overall, understanding the behaviour of free metal ions and their interactions with co-occurring pollutants is crucial for accurately assessing and managing the ecological and health implications of metal contamination in aquatic environments.

In this study, we present a simple and affordable tool based on a functionalized polymeric membrane for measuring the possible interactions of Ni, Cu and Zn with both antibiotics and microplastics. The membrane is composed of a polymer (cellulose triacetate, CTA), an extractant (di-(2-ethylhexyl) phosphoric acid, D2EHPA), and a plasticizer (tributyl phosphate, TBP). The membrane acts as a semipermeable barrier, allowing the selective permeation of divalent metal ions due to the presence of D2EHPA. By using a 0.05 M KNO_3 solution at pH 6 as the feed solution and 0.5 M HNO_3 as the stripping phase, the accumulated divalent metal ion in the receiving phase correlates with free species, as demonstrated when chelating ligands such as EDTA and NTA were added to the feed phase.

When evaluating the possible interactions of metals with other pollutants, we have found that microplastics (using both commercial PVC powder and a blend of waste plastics) did not affected the transport of divalent metal ions through the membrane. However, in the case of antibiotics, a different behavior depending on the sulfonamide and metal was observed. While the addition of SMZ to the water sample did not affected the transport of Ni, Cu or Zn, in the case of SMZ dramatically diminished the accumulation of both Cu and Zn, while Ni was not affected. Therefore, our findings suggest that SMZ in water interacts with Cu and Zn, affecting their availability as free metal ions.

Acknowledgements
This work has been supported through the project PID2022-140312NB-C22 funded by MCIN/ AEI/10.13039/501100011033/ FEDER, UE. N. K. would like to thank the University of Girona for the research fellowship ref. IFUdG 2022.

Here, There and Everywhere - Sustainable Solutions for Liquid Chromatography

O-4

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Keywords: *Alternative mobile phases**,** Automation, Liquid chromatography, Miniaturization*

The solvent consumption in classical liquid chromatography is a critical parameter when it comes to evaluating the sustainability of the analysis method. Not only the type of solvent and its toxicology, but also its disposal, are important. Although the possibilities of miniaturization reduce solvent consumption, they also negatively affect the robustness of the separation method. Therefore, alternative, more sustainable solvents are investigated for the use in liquid chromatography. Another interesting option is carbon dioxide in supercritical fluid state as mobile phase in chromatography. It offers advantages especially in the separation of polar analytes.

In practice, however, it is not the solvent consumption of the mobile phase that is the driving factor in liquid chromatography, but rather the amount of solvent needed for sample preparation and the preparation of accurate dilutions for calibration standards.

Our presentation will focus on holistic concepts of sustainable liquid chromatography and the development of all-encompassing solutions, as well as partial solutions concerning the saving and sustainability of solvents in liquid chromatography. These solutions cover types of solvents, separation columns and column dimensions, as well as separation and elution modes. The suitable planning of chromatographic experiments as well as training of laboratory personnel are also considered, evaluated, and presented as factors in the complete solution for an industrial liquid chromatography laboratory.

Automated Preparation and Analysis of Dried Blood Spot Samples Collected by Volumetric Microsampling

O-5

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Keywords: *3D printing, Automation, Capillary electrophoresis, Dried blood spot, Sequential injection*

The golden standard in clinical analysis is blood plasma obtained by centrifugation of venous blood. Recently, dried blood spot (DBS) samples, collected as capillary blood by a considerably less invasive finger- or heel-pricking, has become a viable alternative to venous blood. Despite numerous benefits for patients and laboratory staff, the use of DBSs has also its drawbacks, particularly associated with their analysis (haematocrit effect and spot non-homogeneity) and preparation (labour- and time-extensive manual sample pretreatment).

As various haematocrit levels in blood samples and non-homogeneous blood distribution within DBSs might have a direct consequence on quantitative analyses of DBSs collected on standard DBS sampling cards [1], simple, flexible, and user-friendly volumetric microsampling devices were recently introduced for precise and accurate DBS collection. These devices are now commercially available in various formats, transfer a pre-defined and exact blood volume onto a sampling sorbent, employ the whole DBS for subsequent preparation and analysis, and have proven to be suitable for remote patient-centric DBS collection and quantitative clinical analysis [2].

The DBS preparation typically requires transformation from the dry to a liquid sample and to mitigate the need for the manual sample preparation, semi-automated and automated instruments became commercially available, which can handle DBS samples collected on the standard sampling cards. However, these instruments are not compatible with the new devices for volumetric DBS microsampling, and analyses of such devices are still based on their manual preparation. Consequently, there is an urgent quest for the development of simple and cheap solutions for unmanned pretreatment and analyses of DBSs collected by the new volumetric devices.

This contribution will discuss two recent solutions developed in our laboratory [3,4] and will summarize fundamentals and the most recent applications of these novel concepts for the automated analyses of DBS samples collected by commercial volumetric microsampling devices. (i) An all-in-one concept (using a single off-the-shelf capillary electrophoresis (CE) instrument) will be presented, which enables automated execution of all tasks of the analytical protocol, including DBS elution, DBS matrix elimination, DBS eluate homogenization, DBS eluate injection, analyte(s) separation, and quantification. (ii) A computer-controlled sequential injection (SI) manifold directly coupled to the CE instrument will be also presented for the automated DBS preparation (using the SI part) and analysis (using the CE part) of the resulting DBS eluates. Different modifications of both concepts, prototyping various 3D-printed flow-through designs for the SI-CE set-up, and their future developments will also be highlighted.

The proposed concepts enabled high-throughput quantitative analyses of DBS samples (> 12 per hour) and their applicability to clinical analysis was exemplified by the determination of several endogenous markers (e.g. amino acids, drugs, and organic ions). Due to the suitability of the volumetric DBS devices for patient-centric blood sampling and of the CE (SI-CE) instruments for their automated analyses, these concepts represent progressive analytical tools for personalized healthcare, screening populations at risk, and can be also useful in remote medicine (e.g. telemedicine). Besides, they can be easily extended to the determination of a wide range of analytes in various dried biological materials and might, thus, play an important role in clinical, toxicological, and forensic analyses in the future.

Acknowledgements

Financial support from the Czech Science Foundation (Grant No. 23-05972S) and the Czech Academy of Sciences (Institute Research Funding RVO:68081715) is gratefully acknowledged.

References

[1] P.M. De Kesel, N. Sadones, S. Capiau, W.E. Lambert, et al., Bioanalysis 5 (2013) 2023-2041.
[2] J. Rudge, S. Kushon, Bioanalysis 13 (2021) 0102.
[3] L. Ryšavá, M. Dvořák, P. Kubáň, Angew. Chem. Int. Ed. 60 (2021) 6068−6075.
[4] M. Dvořák, M. Miró, P. Kubáň, Anal. Chem. 94 (2022) 5301−5309.

Analysis of Volatile Methylsiloxanes in Several Environmental Matrices at LEPABE

O-6

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Keywords: *Environmental matrices, Green analytical chemistry, Volatile methylsiloxanes*

Volatile methylsiloxanes (VMSs) are synthetic chemicals based on silicon-oxygen bonds (see example in **Figure 1**) that are profusely used in industrial and consumer products due to their extraordinary properties [1]. Consequently, their presence in the environment has been a subject of study in recent years, making VMS part of the group of Chemicals of Emerging Concern (CECs). Their ubiquity has been documented in numerous environmental matrices [2] and there is the need to develop reliable analytical protocols for a proper quantification. Whereas the chromatographic identification (mostly by GC-MS) is relatively simple compared to other organic micropollutants, the main challenge resides in the possibility of external contaminations, since even some GC-MS parts like columns and septa have VMSs in their constitution [3]. Also, being of a volatile nature, their analysis in aqueous matrices poses more problems due to their low solubility.

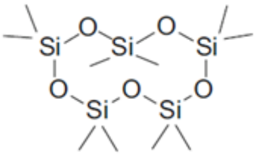

Figure 1. Molecular structure of (D5) the most studied volatile methylsiloxane in the environment

This work intends to give an overview of the analytical solutions found within our group (LEPABE) for the quantification of VMSs in several environmental compartments such as air, soil, vegetation, and water matrices. There will be a focus on the efforts to develop more expedite and at the same time more environment-friendly protocols. **Table 1** summarizes the current protocols in use at the Laboratory for Process Engineering, Environment, Biotechnology and Energy (LEPABE) for the analysis and quantification of VMSs.

Table 1. Current methodologies at LEPABE for the analysis of VMSs

Air	Passive air sampling with XAD-2 and SPE extraction with hexane followed by GC-MS
Biogas	Collection in Tedlar bags and direct analysis in a GC-IMS-SILOX chromatograph
Soil	USE-aided Quechers with hexane/dichloromethane followed by GC-MS
Vegetation	USE-aided Quechers with hexane/dichloromethane followed by GC-MS
Wastewater	USE-aided LLE with hexane followed by GC-MS
Sludge	USE-aided LLE with acetone/hexane (liquid) followed by GC-MS USE-aided Quechers with a sequential hex-hex/dcm-hex/ethyl acetate extraction (soild) followed by GC-MS

Acknowledgements
This work was financially supported by: (i) national funds through FCT/MCTES (PIDDAC) - LEPABE, UIDB/00511/2020 (DOI: 10.54499/UIDB/00511/2020) and UIDP/00511/2020 (DOI: 10.54499/UIDP/00511/2020) and ALiCE, LA/P/0045/2020 (DOI: 10.54499/LA/P/0045/2020); (ii) Agenda "Embalagem do Futuro | + ECOLÓGICA + DIGITAL + INCLUSIVA", nr. C644931699-00000042, investment project nr. 59, financed by the Recovery and Resilience Plan (PRR) and by European Union - NextGeneration EU. V. Homem thanks national funds through FCT, under the Scientific Employment Stimulus-Individual Call – CEECIND/00676/2017 (https://doi.org/10.54499/CEECIND/00676/2017/CP1399/CT0004). N. Ratola thanks FCT for the financial support of his work contract through the Scientific Employment Stimulus - Institutional Call (CEECINST/00049/2018/CP1524/CT0007; https://doi.org/10.54499/CEECINST/00049/2018/CP1524/CT0007).

References
[1] V. Homem, D. Capela, J.A. Silva, A. Cincinelli, L. Santos, A. Alves, N. Ratola, Sci. Total Environ. 579 (2017) 506-513.
[2] K. Kumari, A. Singh, D. Marathe, Environ. Sci. Pollut. Res. (2023).
[3] F. Chainet, C.-P. Lienemann, M. Courtiade, J. Ponthus, O.F.X. Donard, J. Anal. At. Spectrom. 26 (2011) 30-51.

Analysis of PFAAs and Fluorotelomer Alcohols in Shower Curtains: Focus on Migration Conditions

O-7

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Keywords: *Fluorotelomer alcohols, Migration, Persistent pollutants, Pfaas, Textiles*

Perfluorinated compounds (PFCs) are a wide group of chemicals used in a large variety of consumer products such as metal plating, firefighting foams, inks, clothing, textiles and food packaging materials [1]. They are commonly used in the textile industry to impart stain resistance, water resistance, and durability to fabrics. Manufacturers apply PFCs to textiles through various methods such as spraying, dipping, or coating during the finishing process. These compounds form a protective layer on the fabric surface, preventing liquids and stains from penetrating the fibers. This is particularly desirable for outdoor clothing, upholstery, carpets, and shower curtains that may be exposed to moisture or spills [2]. However, concerns have been raised about the environmental and health impacts of PFCs. Per- and Polyfluoroalkyl substances (PFAAs) in particular perluoroalkyl carboxylic acids (PFCA) and perluorosulfonic acids (PFSA) are among the most studied and detected PFCs in the environment and have attracted scientific, regulatory, and public interest because of their long-term persistence, bioaccumulation in the environment, developmental toxicity, and other health effects [3].

Fluorotelomer alcohols (FTOHs) belong to less-polar PFCs and are important precursors of PFCA [4]. They are also used as raw material in various industrial applications due to their water and oil repellent characteristics. However, exposure to FTOHs has also been linked to adverse health effects in humans and animals. In particular, 4:2 FTOH, 6:2 FTOH, 8:2 FTOH and 10:2 FTOH attract the greatest concerns since are the common precursors of some of the best-known PFCAs, namely perfluoro-n-decanoic acid (PFDA), perfluoro-nonanoic acid (PFNA), perfluoro-n-octanoic acid (PFOA), perfluoro-n-heptanoic acid, and perfluoro-n-hexanoic acid (PFHxA) [5].

For this reason, it is very important to carry out studies to assess the presence of these compounds that may in this way represent a source of exposure to the general population. However, a very important aspect is also given by the conditions in which the analyses are carried out and the specific extraction conditions for later analyzing the concentrations of these compounds. Very often the analyses do not take into account the actual conditions of exposure or use and therefore the data obtained are not representative of the real possible exposure problem for humans [6]. There are also no comparative studies in which various PFCs migration conditions are benchmarked.

In this work, 22 PFAAs and 4 FTOHs were analysed in 20 shower curtain samples taken from the Swiss market. Four different types of migration media were considered i.e., organic solvent, water, washing water, mixtures of water and shower gel. Different exposure conditions also in terms of time and temperature of exposure were compared. The extraction and analytical method for PFAAs and FTOHs were optimised to obtain recoveries between 70 and 130% and LOQs between 0.6 and 0.06 μg/Kg. Analyses were performed with LC/MS-MS and GC-MS for PFAAs and FTOHs respectively. The results show a great difference in detection especially for FOTHs depending on the exposure conditions. For this reason, it is very important to assess and take into account the conditions of exposure when implementing regulations and migration limits.

References

[1] D. S. Drage, M. Sharkey, H. Berresheim, M. Coggins, S. Harrad, Rapid Determination of Selected PFAS in Textiles Entering the Waste Stream. Toxics 2023, 11 (1), 55.

[2] S. Schellenberger, I. Liagkouridis, R. Awad, S. Khan, M. Plassmann, G. Peters, J.P. Benskin, I.T. Cousins, An Outdoor Aging Study to Investigate the Release of Per- And Polyfluoroalkyl Substances (PFAS) from Functional Textiles. Environ. Sci. Technol. 2022, 56 (6), pp. 3471-3479.

[3] S. E. Fenton, A. Ducatman, A. Boobis, J. C. DeWitt, C. Lau, C. Ng, J.S. Smith, S.M. Roberts, Per- and Polyfluoroalkyl Substance Toxicity and Human Health Review: Current State of Knowledge and Strategies for Informing Future Research. Environ. Toxicol. Chem. 2021**,** 40 (3), pp. 606-630.

[4] M. Schlummer, L. Gruber, D. Fiedler, M. Kizlauskas, J. Müller, Detection of fluorotelomer alcohols in indoor environments and their relevance for human exposure. Environ. Int. 2013, 57-58, pp. 42-49.

[5] X. Liu, Z. Guo, E.E. Folk, N. F. Roache, Determination of fluorotelomer alcohols in selected consumer products and preliminary investigation of their fate in the indoor environment. Chemosphere 2015, 129, pp. 81-86.

[6] A. Ramírez Carnero, A. Lestido-Cardama, P. Vazquez Loureiro, L. Barbosa-Pereira, A. Rodríguez Bernaldo de Quirós, R. Sendón, Presence of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in Food Contact Materials (FCM) and Its Migration to Food. Foods (Basel, Switzerland) 2021, 10 (7).

SMART: Sustainable Membranes as Affordable and Reliable Tools for Environmental Monitoring of Pharmaceuticals

O-8

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Keywords: *Membranes, Organic contaminants, Sample treatment, Thin-film microextraction*

The occurrence of organic contaminants, particularly steroid hormones and antimicrobials, in aquatic environments is a global threat due to the growing evidence of adverse effects, such as the endocrine disrupting activity and the selection and spread of multidrug resistant bacteria and genes. Sensitive and accurate monitoring studies are a challenge with important but also conflicting aspects, since they help to detect the presence of such pollutants even at very low concentrations, but at the same time they may have inherent environmental impact due to the resources involved. Recent trends pursue the goal of the sustainability by simplifying sample treatments and introducing sorbent-based microextraction. The development of new extraction phases that provide improved selectivity, analyte uptakes capability and recovery, with improved discrimination of matrix interferences, is one of the most active aspects in the evolution of sorbent-based microextraction [1,2]. In such a scenario, the use of membranes or thin films as sorptive phases has gained much more attention as it makes the sample treatment easier in the setup by simply suspending the film in the solution (first the sample and then the eluting solvent) and recovering it with tweezers, without the need for additional steps [3]. To this sense, the focus of this work is the synthesis of efficient and green polymeric membranes for the thin film microextraction (TF-ME) of antimicrobials, namely fluoroquinolones, tetracyclines, macrolides, diaminopyrimidines and glycopeptides, and steroid hormones, namely oestrogens, progestins, androgens and glucocorticoids. In order to minimize the dependence on fossil resources and to avoid the use of plasticizers as active extractant, the membranes developed here have been embedded with bio-based carbon materials derived from waste, in agreement with the 2nd and 3rd principles of green sample preparation [1]. Different polymers (cellulose triacetate and polycaprolactone) have been tested in the role of smart support, evaluating not only the stability of the membrane during the extraction procedure but also the potential for biodegradability after use, which led to the selection of polycaprolactone. Among the wastes, biomass is the most available, inexpensive, non-toxic, and environmentally friendly precursor for carbonaceous materials, namely biochar (BC) or biomass activated carbon (BAC). In this work, a wood-derived BC (Cabot®) and a wood-derived BAC (Nuchar®) have been tested as carbon precursors with the added benefit of extending the life-cycle. The films are home-made prepared, studying different compositions based on the solvent used to solubilize the polymer, and type and amount of char entrapped in the polymeric matrix. The preliminary TF-ME tests make it possible to evaluate the extraction efficiency (EE%) at different times (5 min ÷ 24 h) for each membrane. The use of acetic acid causes a partial acid hydrolysis of the lactone ring making the membrane less stable and therefore less efficient; thus chloroform has been chosen despite its toxicity which is mitigated by its low consumption (1 mL). The adsorption capacity of the neat polymer was negligible (EE% < 8%) for almost all analytes (except for oestrogens and progestins, EE% ≈50%), but it increased significantly in presence of Nuchar® (15%w/w, EE% ≥ 60% at 8h). This biochar possesses a higher affinity in respect to Cabot® (15% w/w, EE% < 15% at 8h) ascribable to the different functional groups and surface area. The results also show that the extraction efficiency is strictly dependent on the amount (15-30% w/w) of Nuchar® incorporated in the polymeric matrix, and finally the film with 24% of Nuchar® has been chosen as it guarantees quantitative extraction of all compounds in 4h. Different elution conditions, i.e. type and volume of solvent, type and time of stirring are being studied together with the analytical evaluation of the method in river and wastewater samples.

Acknowledgements

The Authors acknowledge support from the Ministero dell'Università e della Ricerca (MUR) and the University of Pavia through the program "Dipartimenti di Eccellenza 2023–2027". This work has been supported through the project PID2022-140312NB-C22 funded by MCIN/ AEI/10.13039/501100011033/ FEDER, UE.

References

[1] Á.I. López-Lorente, F. Pena-Pereira, S. Pedersen-Bjergaard, V.G. Zuin, S.A. Ozkan, E. Psillakis, The ten principles of green sample preparation., Trend. Anal. Chem. 148 (2022) 11653.
[2] D. A. Vargas Medina, A. Timoteo Cardoso, E. V. Soares Maciel, F. M. Lanças, Current materials for miniaturized sample preparation: Recent advances and future trends, Trend. Anal. Chem. 165 (2023) 117120.
[3] F. Merlo, A. Profumo, C. Fontàs, E. Anticò, Preparation of new polymeric phases for thin-film liquid phase microextraction (TF-LPME) of selected organic pollutants. Microchem. J. 175 (2022) 107120.

On-site Quantitation of BTEX in Atmospheric Air Using Solid-Phase Microextraction and Gas Chromatography with Photoionization Detector

O-9

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Keywords: *Air analysis, BTEX, Gas chromatography, Solid-phase microextraction*

Air pollution with benzene, toluene, ethylbenzene and xylenes (BTEX) cause major health risks and should be monitored. Existing methods of BTEX determination in air are based on gas chromatography (GC) with mass spectrometric (MS) and other types of detectors. Most difficult stages of such analyses are sampling, sampling preparation and calibration. Direct determination of BTEX in atmospheric air using GC is impossible without preconcentration of the analytes. Existing methods based on solid-phase microextraction (SPME) allow simple and accurate BTEX quantitation with a standard addition calibration [1]. For faster results and better accuracy, Koziel et al. [2] developed the method for on-site BTEX quantitation using portable GC. However, the calibration for this method requires a standard gas generator and traceable certified permeation tubes.

The purpose of this study was to simplify the method of Koziel et al. [2] for the on-site quantification of BTEX in atmospheric air using the SRI 8610C GC with photoionization detector (PID) and apply it in the town of Talgar, Almaty oblast, Kazakhstan. Air was collected to four replicate 250 mL gas sampling bulbs, and standard addition method was used for on-site calibration using one of the collected replicates (**Figure 1**). The simplified method did not require a standard gas generator and traceable certified permeation tubes for instrument calibration. The inlet of SRI 8610C GC was modified to work with 78.5 mm × 6.5 mm liners and allow faster and more efficient desorption of analytes from the fiber and their transfer to the column. The method was tested twice in February (average sampling temperature from -20 to -12 °C) and twice in March (+12 to +13 °C), 2024 using extraction times 5 and 15 min, respectively. Before an extraction, gas sampling bulb with collected air was located in the thermostat heated to 40 °C for 10 min, and depressurized to minimize the effect of pressure on accuracy of the measurements.

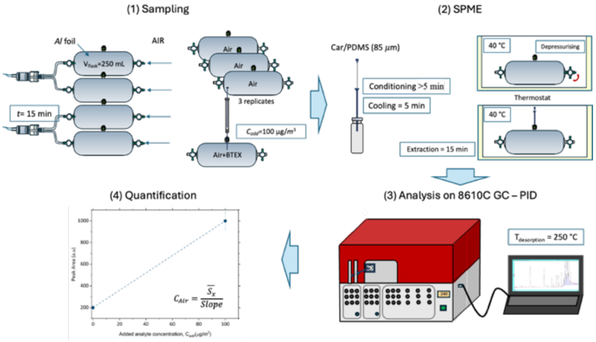

Figure 1. Schematic representation of the developed method.

In February, only benzene (14.8 and 5.6 µg/m^3) and toluene (12.7 and 7.0 µg/m^3) were detected, most probably, due to the insufficient extraction time and low concentrations of ethylbenzene and xylenes. In March all analytes were detected, except ethylbenzene in one sample. Benzene concentrations were 11.3 and 6.7 µg/m^3, toluene – 21 and 4.9 µg/m^3, ethylbenzene – 5.0 µg/m^3, m-/p-xylenes – 3.3 and 1.9 µg/m^3, o-xylene – 6.2 and 9.6 µg/m^3. Limits of detection (LODs) for benzene, toluene, ethylbenzene, m-/p-xylenes and o-xylene were 0.06, 0.3, 2, 0.8 and 2 µg/m^3, respectively. The developed method is simple, accurate and can be recommended for quick on-site quantitation of BTEX in atmospheric air. Standard addition calibration allows quick re-calibration of the instrument and matrix effects control.

Acknowledgements

This research was funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP14871374).

References

[1] N. Baimatova, B. Kenessov, J.A. Koziel, L. Carlsen, M. Bektassov, O.P. Demyanenko, Simple and accurate quantification of BTEX in ambient air by SPME and GC-MS, Talanta 154 (2016) 46–52.

[2] J. Koziel, M. Jia, A. Khaled, J. Noah, J. Pawliszyn, Field air analysis with SPME device, Anal Chim Acta 400 (1999) 153–162.

Paper-based Electroanalytical Devices Equipped with CO_2 Laser-Assembled Nanostructured Conductive Films

O-10

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Keywords: *Electrochemical sensors, Electroanalytical application, Laser-induced nanomaterials, Paper-based analytical devices, Sensors*

Nowadays, a renewed interest is directed to paper-based point-of-care/need devices. Cellulosic substrates offer useful features including flexibility, capillarity, and porosity resulting prone to analytical device development. On the other hand, paper, in addition to being available worldwide and environmentally friendly, is potentially functionalizable with different types of nanomaterials (NMs) and offers compelling microfluidics opportunities without the need for sophisticated equipment. However, NMs synthesis and integration into lab-made paper-based sensors and analytical devices (PAD) still represent a critical issue. To overcome tedious, expensive, and not sustainable conventional fabrication techniques, several efforts are devoted to implementing effective and affordable technologies to produce nano-equipped paper sensors and PAD. In this framework, CO_2 laser-based technologies represent a captivating opportunity.

This presentation will be focused on the production of different functional nanostructured films via CO_2-laser plotter and their integration within completely lab-made sensors and PAD, with the idea of reducing the use of solvents/chemical compounds as much as possible and generating virtuous circles from an environmental and economic point of view. In particular, an overview of the (i) development of freestanding laser-induced nanostructured films [1] and their integration into sensors and PAD will be given. Particular attention will be paid to nanostructured surface solvent-free production and nano/micro-architectures assembling, and (ii) fabrication of disposable paper devices using low-cost/sustainable substrates (i.e., nitrocellulose, paper, recycled paper, paper produced from wastes, etc.) via benchtop microfabrication technologies such as stencil-printing, cutter-plotting, CO_2-laser molding, thermal-lamination, etc.

The exploitability of the developed devices will be demonstrated for the analysis of agri-food quality and safety markers, and biological interest compounds in model solutions and real samples. Among others, will be presented: (i) electrochemical sensors based on laser-induced reduced graphene oxide (rGO) films integrated into different recycled papers and paper produced from wastes able to determine different analytes in different samples (food, supplements/medicines, urine), (ii) an integrated paper/graphene 3D pop-up device for the quantitative sensing of carbaryl in grains at EU-law limits [2] and (iii) a laser-nano decorated electrochemical lab-on-strip device for the rapid pretreatment-free evaluation of antioxidant capacity in extra virgin olive oil; (iv) a laser-assembled conductive 3D nanozyme film-based paper sensor for real-time detection of H_2O_2 released from cancer cells will be also shown together to possibly additional findings concerning other electroanalytical sustainable PADs.

This presentation aims to prove how CO_2-laser plotter-based technologies are able to generate nanostructured sensing surfaces that can be integrated trought benchtop technologies in paper-based substrates, opening new paths for the development of on-demand sustainable analytical devices able to ensure the required performances.

Acknowledgements
This research was funded by the European Union – Next Generation EU. Project Code: ECS00000041; Project CUP: C43C22000380007; Project Title: Innovation, digitalization and sustainability for the diffused economy in Central Italy - VITALITY

References

[1] F. Della Pelle, Q. U. A. Bukhari, R.A. Diduk, A. Scroccarello, D. Compagnone, A. Merkoçi, Nanoscale 15(15) (2023) 7164-7175.
[2] S. Fiori, A. Scroccarello, F. Della Pelle, M. Del Carlo, D. Compagnone, Sensors and Actuators B: Chemical 399 (2024)134768.

Immobilization of Metal-Organic Frameworks in 3D Printed Devices for the Development of Fluorescent and Colorimetric Sensors Used in the Detection of Antibiotics and Heavy Metals

O-11

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Keywords: *Colorimetric sensor, Fluorescence sensor, Metal-organic framework, On-site analysis, 3D-printed device*

Metal-organic frameworks (MOFs) are widely known for their use in the adsorption and detection of various contaminants. For analytical applications, MOFs are promising substrates for producing fluorescent and colorimetric sensors [1]. In previous works, various techniques have been developed for immobilizing MOF in 3D printed devices to provide robust and adaptable supports for the extraction and preconcentration of analytes. The Stick & Cure technique and the Post-Printing technique are the most commonly used methods. The first involves coating the device with the material before UV curing, and the second involves coating the device drop by drop with a mixture of the material with a polymer [2,3]. According to initial experiments in the development of MOF-based sensors, these techniques did not yield a homogeneous layer of MOF on the 3D printed device, potentially hindering precise analysis. To address this drawback, our group presents a new technique for immobilizing MOFs in 3D printed devices (a modification of the post-printing technique) for use in developing fluorescent and colorimetric sensors for the detection of tetracyclines and arsenite, respectively.

Inappropriate use of Tetracyclines (TC) and Arsenite (As(III)) can lead to adverse effects on health and the environment. TC can cause antibiotic resistance, while As(III) is considered a toxic element and a dangerous contaminant [4,5]. Therefore, rapid, selective, sensitive and on-site analysis is of great interest in research to guarantee health safety and estimate environmental contamination. We present the development of two different works utilizing the proposed immobilization technique. In the first work, a fluorescent sensor has been developed for visual and rapid detect of TC in water samples. A europium-based metal-organic framework (Eu-MOF) was synthesized using a facile and environmentally friendly methodology, which was then immobilized in the wells of a 3D-printed microplate by mixing the lanthanide MOF with the polymer polyvinylidene difluoride (PVDF). Optimization of the mixing percentages (Eu-MOF/polymer) resulted in a hydrophobic coating with high fluorescence emission, enabling multisample analysis with good selectivity and notable device recyclability. The proposed Eu-MOF sensor exhibited strong and stable red fluorescence emission, with fluorescence quenching immediately observed upon contact with TC. In the second work, a 3D millifluidic device was constructed for the in-situ determination of As(III) using the hydride generation technique. For this purpose, the As(III) present in the sample was reacted with HCl and a reducing agent ($NaBH_4$), producing arsine (AsH_3), a volatile hydride that, upon contact with a sensor supporting the Ag-BTC MOF in a 3D printed part, generates silver (Ag) nanoparticles, causing a color change from white to dark brown depending on the concentration of As(III). The millifluidic device consists of an injector for the sample and reducing agent, a well for hydride generation, and the detection zone: a cap coated with the Ag-BTC MOF using the proposed immobilization technique. For detection in both applications, a portable 3D-printed platform that uses a lamp (UV or white light, depending on the case) as a radiation source and a smartphone for photographing was built. Captured images were analyzed using ImageJ software to determine RGB color intensities. Under optimized conditions, the proposed sensors show promise for reliable and real-time detection of contaminants in aqueous samples.

Acknowledgements

The authors acknowledge financial support from project PID2019-107604RB-I00 MICIU/AEI/10.13039/501100011033. M.A.V-M. acknowledges the support from the Spanish Ministerio de Educación y Ciencia for the pre/post-doctoral research fellowship (FPU19/06082).

References

[1] Z. Zhang, Y. Zhang, H. Jayan, S. Gao, R. Zhou, N. Yosri, X. Zou, Z. Guo, Recent and emerging trends of metal-organic frameworks (MOFs)-based sensors for detecting food contaminants: A critical and comprehensive review, Food Chem. 448 (2024) 139051.

[2] M.A. Vargas-Muñoz, C. Palomino, G. Turnes, E. Palacio, 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, J. Environ. Chem. Eng. 11,5 (2023) 110503.

[3] D. Barzallo, A. Están, N. Crespí, C. Palomino, G. Turnes, E. Palacio, L. Ferrer, On-site extraction using a 3D printed device coated with Zn/Co-ZIF-derived carbon followed by an on-line SIA-HPLC-FL system for fluoroquinolones determination in wastewater, Talanta. 273 (2024) 125897.

[4] F. Ahmadijokani, Hossein Molavi, S. Tajahmadi, M. Rezakazemi, M. Amini, M. Kamkar, O.J. Rojas, M. Arjmand, Coordination chemistry of metal–organic frameworks: Detection, adsorption, and photodegradation of tetracycline antibiotics and beyond, Coord. Chem. Rev. 464 (2022) 214562.

[5] C. Zong, X. Jin, J. Liu, Critical review of bio/nano sensors for arsenic detection, Trends Environ. Anal. Chem. 32 (2021) e00143.

Greening Electrochemical (EC) Analysis & Biosensing: From EC Mini-cell to Sustainable EC Sensor Solutions

O-12

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Keywords: *Green analytical chemistry, Green chemistry, Green electroanalysis, Green biosensing, Green voltammetry*

The high-tech scheme options of modern voltammetry, amperometry and electrochemical biosensing are since decades among the powerful pillars of advanced industrial, clinical, pharmaceutical, food and environmental analysis. For the very diverse community of applicants of electroanalysis an ecologically aware execution of their analytical procedures became in times of environmental pollution concerns, climate change and resource shortness's for obvious reason a ruling mindset for project design and running. Accordingly, the minimization of electrolyte waste with or without toxic ingredients, a careful solvent/electrolyte choice, little as possible analytical reagent consumption, minimization of plastic and/or ceramic sensor strip waste, and a sustainable electrode and biosensor preparation and application with minimal energy and material demand are the criteria to be compliant with, based on the commonly accepted principles of 'Green Chemistry' [1] and 'Green Electroanalysis' [2]. Communicated here will be the concept of an unlimited reusable microliter-volume three-electrode electrochemical cell and the usefulness of the special minicell with respect to sustainability and 'Green Electroanalysis' compliance will be highlighted through the demonstration of success with applications for an electrochemical blood drug monitoring and an advanced electrochemical antibiotic susceptibility testing. Also discussed will be an entirely nanomaterial-free and thus truly green (glucose) biosensor design that, despite of the lack of nanomaterial support, offers an exquisite nanomolar practical limit of (glucose) detection, and cheap and abundantly available stationery pencil leads will be presented as favorable precursors for sustainable electrode fabrication.

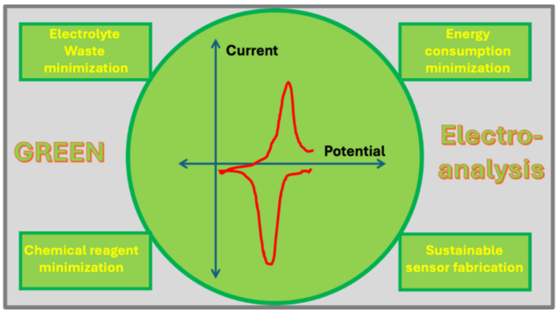

Figure 1. Caption (Arial 8 pt).

Figure 1. The principles of Green Electroanalysis [2].

Acknowledgements
The financial support of VISTEC and of all industrial and governmental sponsors of VISTEC/BSE is acknowledged.

References

[1] P.T. Anastas, Green Chemistry, and the role of analytical methodology development, Crit. Rev. Anal. Chem. 29 (1999) 167-175.
[2] L. Hernández, J.M. Pingarrón, P. Yáñez-Sedeño, Green electroanalysis, in: M. de la Guardia, S. Garrigues (Eds.), RSC Green Chemistry Series: Challenges in Green Analytical Chemistry, The Royal Society of Chemistry, London, 2011, ch. 8, pp. 199-223.

Gel Electro-Membrane Extraction: The Movement from Extraction to Sensing. Application for Fluorescence Detection of Norfloxacin

O-13

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Keywords: *Agarose gel, Electrocolorimetric sensing approach, Electromembrane extraction, Fluorescence, Green chemistry*

Gel electromembrane microextraction (G-EME) has been recently introduced as a green and environmentally friendly extraction method for various types of analytes. G-EME has various advantages over traditional electromembrane extractions, such as the ability to easily fabricate gel membranes of various shapes and thicknesses. Additionally, it allows for the extraction of polar analytes without requiring any complex reaction. Ultimately, the usage of a gel electromembrane extraction system contributes to a high level of environmental-friendliness due to its almost solventless nature. The undesirable electroendosmosis (EEO) flow phenomenon, which happens during the extraction process and affects the volume of the acceptor and donor phases, has been observed to have an impact on G-EME despite its advantages. This has an impact on the extraction and preconcentration efficiency. An innovative integrated sensing strategy based on G-EME and in gel colorimetric detection was created to address these issues. Comparing this integrated technique to traditional G-EME and on-chip EME can reveal various advantages. For instance, fewer extraction and detection procedures are required, the analytical process takes less time overall, the results are more repeatable and sensitive, and the impact of EEO is reduced. This sensing platform was successfully used to measure iodide, Cr(VI), and Ni(II) in different food matrices [1,2]. In order to expand the application of this new sensing system, we tried to apply it for fluorescence detection instead of colorimetric detection. Norfloxacin was chosen as a model fluorescent analyte. A smartphone was used to take the images of gels while ImageJ software was used to analysis the RGB. Under the optimum condition, the obtained LODs was 0.009 mg L^{-1}, which is suitable for the Maximum Residue Limits of the quinolone group in animal products.

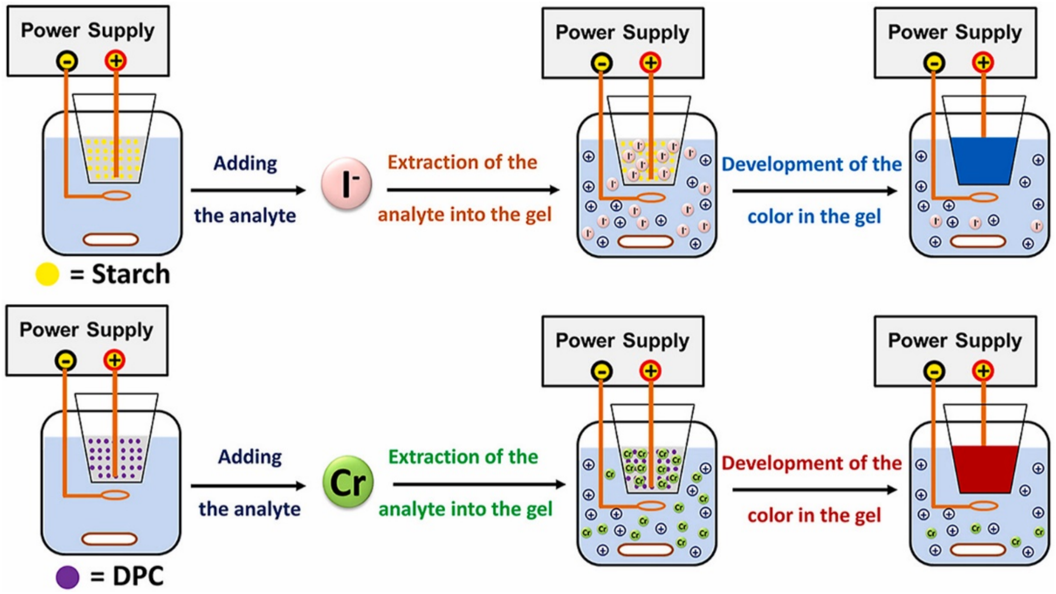

Figure 1. The schematic of working principles of the proposed electrocolorimetric sensing approach.

Acknowledgements

The authors would like to thank the Second Century Fund (C2F), Chulalongkorn University, Thailand, for financial support of this project.

References

[1] A. Sahragard, W. Alahmad, P. Varanusupakul, Electrocolorimetric gel-based sensing approach for simultaneous extraction, preconcentration, and detection of iodide and chromium (VI) ions, Talanta 235 (2021) 122715.
[2] A. Sahragard, W. Alahmad, P. Varanusupakul, Application of electrocolorimetric extraction for the determination of Ni(II) ions in chocolate samples: a green methodology for food analysis, Food Chem. 382 (2022) 132344.

Natural Deep Eutectic Solvent-Based Liquid Phase Microextraction in a 3D-Printed Microfluidic Flow Cell for the On-Line Determination of Thiabendazole

O-14

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Keywords: *Liquid phase microextraction, 3D-printing, Microfluidic flow cell, NADES, Thiabendazole*

In this work, a 3D-printed microfluidic flow cell was used for the natural deep eutectic solvent (NADES)-based liquid phase microextraction coupled to fluorescence detection of thiabendazole in juice samples. The microfluidic flow cell was 3D printed by stereolithography and consisted of two patterned plates, each containing a microchannel (acceptor and donor channel). The microchannels were separated by a polypropylene membrane impregnated with the corresponding NADES, thus acting as supported liquid membrane (SLM). Among the NADES investigated, formic acid:L-menthol (molar ratio 1:1) was selected as SLM, avoiding the use of conventional organic solvents. The influence of microfluidic flow cell geometry, including microchannel length and depth, on analytical performance was investigated. The experimental conditions were optimized and the pH of the donor and acceptor solutions were set to 2 and 12, respectively. The flow-rate of the donor solution was established at 0.22 mL/min for an extraction time of 5 min. The acceptor volume was maintained in static mode. Thiabendazole was on-line determined by fluorescence detection, thus saving time and solvent consumption. The proposed microfluidic device was successfully applied for the determination of thiabendazole in fruit juice samples.

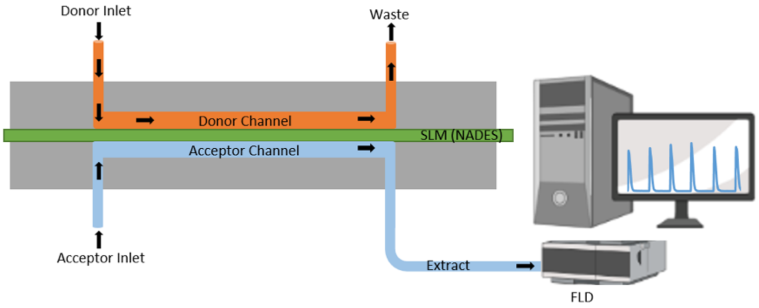

Figure 1. Scheme of the microfluidic flow cell.

Acknowledgements
The Grant PID2021-122327OB-I00 funded by MCIN/AEI/ 10.13039/501100011033 and by "ERDF A way of making Europe" is gratefully acknowledged. This article is based upon work from the National Thematic Network on Sustainable Sample Treatment (RED2022-134079-T) funded by the Spanish Ministry of Science and Innovation, and the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society.

Evaluation of Deep Eutectic Solvents in the Synthesis of Molecularly Imprinted Fibers for the Solid-Phase Microextraction of Triazines in Soil

O-15

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Keywords: *Molecular imprinting, Sample preparation, Solid-phase microextraction, Deep eutectic solvents, Soil*

Nowadays, molecularly imprinted polymers (MIPs) are well established and considered excellent materials for performing selective extractions. However, with the progressive implementation of the Principles of Green Chemistry, it is necessary to search greener alternatives for both the synthesis and further use of MIPs in sample preparation. Accordingly, in the present work, different deep eutectic solvents, DES, (both hydrophilic and hydrophobic), as an alternative to the conventional organic solvents (i.e. toluene), were evaluated as porogen for the synthesis of imprinted fibers (monoliths), using fused silica capillaries as molds, for solid-phase microextraction (SPME).

From this study, the polymer prepared with propazine (dummy template), methacrylic acid (monomer), ethylenglycol dimethacrylate (cross-linker) and a formic acid:L-menthol (1:1) DES (porogen) showed the best performance to selectively rebind triazines. After optimization of the different variables involved in SPME, the new imprinted fibers were successfully applied to the extraction of target analytes (desisopropylatrazine, desethylatrazine, simazine, and atrazine) from soil sample extracts, providing relative recoveries ranging from 75.7 to 120.1 %, reaching limits of detection within the range 6.2-15.7 ng.g^{-1}, depending upon the analyte.

Acknowledgements
The Grant PID2021-122327OB-I00 funded by MCIN/AEI/ 10.13039/501100011033 and by “ERDF A way of making Europe” is gratefully acknowledged. This communication is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society and the National Thematic Network on Sustainable Sample Treatment (RED2022-134079-T) funded by the Spanish Ministry of Science and Innovation.

Greenness of Sample Preparation for Proteomic Analysis

O-16

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Keywords: *Bottom-up, Glycans, Green analytical chemistry, Middle-up, Proteins*

Proteins are essential biomolecules that perform vital functions and provide overall control of all living organisms. Moreover, many proteins have become important biopharmaceuticals [1]. The molecular complexity of these molecules usually requires a combination of multiple sample preparation and analytical approaches to provide their detailed characterization. Liquid chromatography (LC) is a widely recognized work-horse technique for proteomic applications. In response to the current global environmental challenges, some recent LC methods have promoted greener solvents [2]. On the other side, eco-friendly capillary electrophoresis (CE) has become an increasingly popular separation technique in proteomic analysis [3]. It provides fast, highly efficient separations and requires ultralow sample and reagent volumes per single analysis.

Proteomic analysis can be performed at four levels: intact, subunit, peptide, and released glycans. The more traditionally used approach is bottom-up analysis, where proteins are first enzymatically digested into their constituent peptides. The top-down approach, where proteins are analyzed in their intact form (native or denatured), and a middle-up approach with partial enzymatic digestion have become increasingly popular in the recent years, especially for analysis of monoclonal antibodies [4].

The Green Analytical Chemistry (GAC) [5] are general guidelines for greening analytical methods and to address the demands of the analytical field. The first principle of GAC suggests the elimination of sample preparation; However, there is a very limited possibility to incorporate direct analysis in proteomic applications, except perhaps for top-down analysis. Sample preparation methods can be very tedious, time-consuming, and generate (hazardous) laboratory waste. Therefore, the importance of greener sample preparation in analytical methods was addressed in the principles of Green Sample Preparation (GSP). Many cutting-edge sample preparation advances have focused on the implementation of safer and greener solvents and renewable and natural adsorbents in sample preparation approaches, as well as increased throughput, miniaturization, and automation [6].

In this work, various representative approaches for sample preparation for proteomic analysis were evaluated using AGREEprep software and the greenness of several representative analytical methods was assessed by AGREE software [7]. The results show that the trends in GAC method development for proteomic research should focus on the miniaturization of analytical devices and on on-line and in-line sample preparation approaches.

Acknowledgements

The research work was supported by the Scientific Grant Agency of the Ministry of Education, Research, Development and Youth of the Slovak Republic under the project VEGA 1/0514/22 and by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V04-00192. The work is based upon work from the Sample Preparation Study Group and Network supported by the Division of Analytical Chemistry of the European Chemical Society.

References

[1] A. Mullard, FDA approves 100th monoclonal antibody product, Nat. Rev. Drug Discov. 20 (2021) 491–495.
[2] P.I. Napolitano-Tabares, I. Negrín-Santamaría, A. Gutierrez-Serpa, V. Pino, Recent efforts to increase greenness in chromatography, Curr. Opin. Green Sustainable Chem. 32 (2021) 100536.
[3] K. Marakova, M. Opetova, R. Tomasovsky, Capillary electrophoresis-mass spectrometry for intact protein analysis: pharmaceutical and biomedical applications (2018–March 2023), J. Separ. Sci. 15 (2023) 2300244.
[4] J. Giorgetti, A. Beck, E. Leize-Wagner, Y.N. François, Combination of intact, middle-up and bottom-up levels to characterize 7 therapeutic monoclonal antibodies by capillary electrophoresis - mass spectrometry, J. Pharm. Biomed. Anal. 182 (2020) 113107.
[5] A. Gałuszka, Z. Migaszewski, J. Namiesnik, The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices, TrAC, Trends Anal. Chem. 50 (2013) 78–84.
[6] F. Pena-Pereira, I. Lavilla, C. Bendicho, Greening sample preparation: an overview of cutting-edge contributions, Curr. Opin. Green Sustainable Chem. 30 (2021) 100481.
[7] K. Marakova, R. Tomasovsky, M. Opetova, K.A. Schug. Greenness of proteomic sample preparation and analysis techniques for biopharmaceuticals. TrAC-Trends in Analytical Chemistry 171 (2024) 117490.

Multi-Criteria Decision Analysis for Selection of Greener Chemicals for Analytical Chemistry

O-17

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Keywords: *Decision making, Green analytical chemistry, Green solvents, Greenness assessment*

Multi-criteria decision analysis (MCDA) serves as a pivotal tool in managerial decision-making processes, offering a robust framework for making scientifically informed choices. By navigating through a plethora of criteria, often conflicting, MCDA aids in the selection of the most optimal alternative from a multitude of options.

When conventional environmental parameters are employed as criteria, MCDA transforms into a potent instrument for evaluating "greenness" or ecological sustainability. These metrics encompass diverse facets, including the toxicity of compounds across various organisms and exposure pathways, environmental persistence indicators like hydrolysis half-life and biodegradability, as well as safety parameters such as flash point, flammability or the generation of harmful degradation by-products. Through the integration of these dimensions, MCDA facilitates the systematic ranking of alternatives based on their environmental footprint. Given the multifaceted nature of greenness, a multi-criteria approach becomes particularly pertinent.

MCDA has been successfully deployed to assess the ecological impact of a range of substances, spanning from organic solvents to ionic liquids, deep eutectic solvents, and derivatization agents. In each instance, exhaustive rankings were generated, offering insights into the environmental viability of all alternatives. Consequently, actionable recommendations regarding the adoption of environmentally benign solvents and reagents were provided, while simultaneously flagging those warranting avoidance.

Furthermore, MCDA's compatibility with experimental design methodologies enables the simultaneous optimization of both environmental sustainability and analytical process efficiency. This synergy underscores the versatility of MCDA in promoting green chemistry principles within analytical frameworks.

Green Microextraction Techniques for DBPs Monitoring

O-18

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Keywords: *Adsorption, Extraction, HiSorb, Gas chromatography-Mass spectrometry*, *Thermal desorption*

Chemical disinfection, while essential for numerous purposes, inadvertently introduces risks to human health. These risks encompass potential carcinogenic, reproductive, and developmental effects, linked to disinfection byproducts (DBPs) [1]. Fortunately, there are now several green microextraction techniques available for monitoring DBPs, such as stir-bar sorptive extraction (SBSE), high-capacity sorptive extraction (HiSorb), and thin film-solid phase microextraction (TF-SPME) [2]. These modern extraction tools offer advantages over traditional SPME fiber because of their large sorbent volume (μL) and surface area (mm^2) [3]. While TF-SPME appeared promising for analyzing trihalomethanes (THMs), HiSorb was ultimately chosen for DBP analysis because of its automation potential. Consequently, a headspace thermal desorption-gas chromatography-mass spectrometry (HS-HiSorb-TD-GC-MS) method was developed and refined by optimising different parameters such as coating material, volume to liquid headspace, extraction time, extraction temperature, salt addition, and stirring. The respective method was developed to detect and quantify 12 DBPs, based on the method's linearity, limits of detection and quantification (LOD, LOQ), repeatability, and reproducibility. The DBPs that can be analyzed by the headspace HiSorb-TD-GC-MS method, as well as the method validation details, will be presented and discussed.

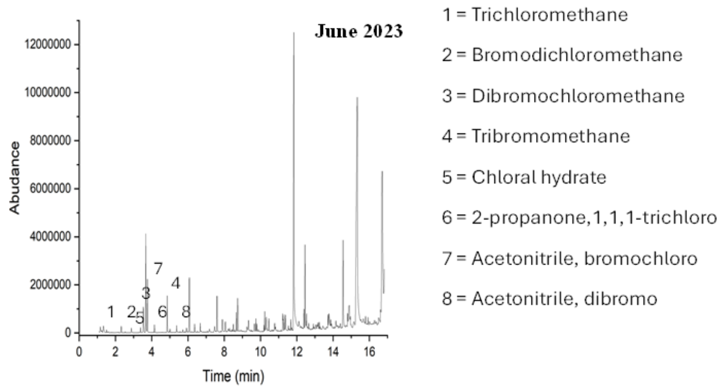

Figure 1. HS-HiSorb-TD-GC-MS chromatogram with compounds detected in a real water sample.

Acknowledgements
This work has received funding from the European Union's Horizon Europe research and innovation program under grant agreement No 101081728, intoDBP: Innovative tools to control organic matter and disinfection byproducts in drinking water. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them.

References

[1] Barcelo, D., Emerging Organic Contaminants and Human Health. In Emerging Organic Contaminants and Human Health, Springer-Verlag Berlin Heidelberg, vol. 20, 2012.
[2] N. Lorenzo-Parodi, W. Kaziur, N. Stojanović, M.A. Jochmann, T.C. Schmidt, Solventless microextraction techniques for water analysis, Trends in Analytical Chemistry 113 (2019) 321-331.
[3] Ouyang, G., Pawliszyn, J., SPME in environmental analysis, Analytical and Bioanalytical Chemistry 386 (2006) 1059-1073.

Assessing Water Quality: Fast, High Sensitivity Analysis of Chlorophenols and Other Common Odorants by Automated HiSorb

O-19

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Keywords: *Chlorophenols, Environmental, GC-MS, Odorants, Water*

Global regulations impose stringent monitoring requirements on wide-ranging volatile organic compounds (VOCs) in water because of the negative impact they pose to human health. Due to differences in volatility or suitability to a particular extraction phase, multiple tests are performed on water samples to analyse the full range of VOCs present. Yet, workflows are often labour intensive, have limited sensitivity or generate large quantities of solvent waste.

Chlorophenols are typically analysed separately to other malodorous compounds present in water, such as geosmin, anisoles and methylpyrazines, and are regulated by various environmental protection agencies such as the US Environmental Protection Agency (EPA), the Korean Ministry of Environment and the European Commission, with the EPA stipulating a limit of 1 µg/L for 5CP in drinking water.[1] Standard methods for detecting chlorophenols including ISO 8615-2:1999 and US EPA method 604 specify liquid-liquid extraction with derivatisation, hence these methods are manual, generate a lot of solvent waste and use harmful derivatising agents.

Here, we investigate immersive high-capacity sorptive extraction (HiSorb) on the Centri with GC-MS analysis and demonstrate a new, highly-sensitive, fully automated method to analyse all odour-causing VOCs in one run. Using laboratory standards in clean drinking water, MDLs well below regulatory requirements were achieved (< 10 ng/L for chlorophenols and < 1 ng/L for other odorants) with excellent reproducibility (< 5% RSD) and linearity ($R^2 > 0.995$), demonstrating a robust and quantitative method, ideal for use in high productivity laboratories. The method remained effective even when extracting from more complex environmental waters containing many other dissolved VOCs. It is anticipated that the method can be applicable to other VOC classes too.

Thanks to its large sorptive phase HiSorb allowed highly-sensitive analysis with simple sample preparation, all without generating solvent waste. With the addition of DVB and CWR phases, analyte extraction and thus, GC-MS response, increased up to 70-fold for the chlorophenols specifically. Analyte preconcentration on Centri's backflushed, cryogen-free focusing trap prior to GC injection enhances sensitivity of HiSorb analysis further to reach the low ng/L concentrations required. Backflush trap operation was important here to enable wide-ranging compounds to be assessed in a single analytical run. Sample overlap ensured high throughput with approximately 36 samples analysed per day per GC/MS system.

References

[1] Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Pentachlorophenol (Update) (Draft). Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA. 1999.

SBSE to Overcome Analytical Challenges for Next-Generation Product Registration

O-20

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Keywords: *Ecotoxicological testing, Gas chromatography, REACH, SBSE*

If you manufacture or import one tonne or more of a chemical substance into the European Economic Area per year, you must record this in the REACH database. Under the REACH Regulation, the manufacturer and/or importer is responsible for assessing the application-specific risk posed by chemicals and providing relevant safety information to users.

An accurate assessment of environmental hazards and risks is based on the analysis of the effects of chemicals on aquatic organisms. In regulatory studies, it is imperative to analytically verify the exposure of organisms to substances and measure their concentrations within test systems. This information is crucial for understanding the acute or chronic effects of chemicals on aquatic organisms.

The increasing requirements for product registration and the increasing complexity of next-generation products require advanced analytical techniques with careful sample preparation. Traditional liquid/liquid extraction methods used for gas chromatographic analysis have limited sensitivity due to dilution and require significant amounts of hazardous solvents.

To increase sensitivity and minimize solvent consumption, alternative sample preparation such as Stir Bar Sorptive Extraction (SBSE) was investigated to replace traditional liquid-liquid extraction. By optimizing the method parameters, a significant increase in sensitivity (>100x) could be achieved, while at the same time safety and resource conservation were promoted by replacing solvents with a reusable adsorbent.

The optimized method was used to control concentrations in ecotoxicological tests.

Use of the Cold Block Digestion Technique for Multi-Element Analysis of Geological Samples

O-21

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Keywords: *Cold block, Geological samples, Strong acid digestion*

Sample digestion is a critical step in the geochemical analysis. It directly affects the quality of the analytical results, and it is one of the most important prerequisites for obtaining reproducible and accurate results. [1] Although there have been many developments in the sample digestion procedures, the digestion remains one of the most complex areas in the analytical procedure. Selection of the most appropriate digestion type depends on the analytes of interest, their levels, the analytical technique used, the mineralogical composition of the sample, the sample size, required sample throughput as well as the related reagent and labor cost and consumption. [2] Laboratory's safety and environmental aspects have also gained a lot more attention in the recent years putting the emphasis on minimal analysts' exposure and minimum environmental emissions.

Complete digestion of geological samples remains one of the most difficult digestions. "Near total digestion requires the use of a combination of strong mineral acids (HCl, HNO_3, $HClO_4$ and HF), long digestion times and/or high temperatures. These digestions are taken to incipient dryness which requires close attention from the analyst and well controlled heating temperatures. The use of perchloric acid presents high explosion risk, requires high evaporation temperatures and special fume hoods fitted with the expensive wash down safety systems.

Use of Cold Block technology offers a possibility to overcome many of the above concerns through much faster, simpler and safer digestions of the geological samples. Direct transmitting of the focused short wavelength infra-red radiation to the particle, rather than heating the acid-sample mixture (such as in the classical digestion methods) provides much faster heating of the sample. [3] This, in combination with the unique "cooling" (condensation) zone provides much faster digestions improving the TAT while at the same time limiting the analyst's acid exposure. The CB digestions are simple computer-controlled digestions that take on average 10-45 min to digest the sample (compared to the classical hot plate and hot block digestions that can take up to couple of hours. The CB strong acid digestion utilizes a mixture of 3 acids (HCl, HNO_3 and HF) with no need for perchloric acid, significantly lowering the risks associated with its use. Efficient condensation in the "cooling "zone (maintained at -5^0C) significantly reduces the amount of acid fumes released. Basic principle of the operation is presented in the below Figure.

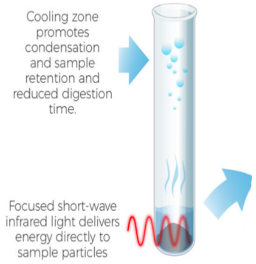

Figure 1. Cold Block working principle.

Digestion of various geological certified reference materials (CRMs) using CB technique provided results comparable to the classical 4 acid digestion techniques for multi-element analysis and across various materials such as Cu and Co ores, Li ores, Zn, Pb ores, some tailing as well as soils. Solutions were read on the ICP-OES and ICP-MS against matrix matched calibration standards. Good repeatability was obtained (evaluated on 7 replicates and using %RSD and squared Chi test) across various CRMs and elements. Although, the use of boric acid to neutralize remaining HF and to re-solubilize some of the fluorides after the digestion, results in the increase of some of the detection limits (compared to the classical 4 acid digestion method0, the detection limits remain at low ppm range. However, with no need to bring the sample to the "incipient dryness", the digestion is significantly shortened and the analyst's exposure to the acid is minimal. The possibility of "baking" of the sample during the drying process and loss of some of the elements due to their volatility and limited solubility is also prevented.

References

[1] W. Zhang, Z. Hu, Recent advances in sample preparation methods for elemental and isotopic analysis of geological samples, Spectrochimica Acta Part B. 160 (2019) 105690.
[2] P. J. Potts, P. Robinson, Sample preparation of geological samples, soils and sediments, Comprehensive Analytical Chemistry 41 (2003) 723-763.
[3] Y. Wang, R. Kanipayor, I.D. Brindle, Rapid high-performance sample digestion for ICP determination by ColdBlock digestion, J. Anal. Spectrom. 29 (2014) 162-168.

New Sample Preparation Strategies for the Control of VOC in Wood-Based Panels

O-22

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Keywords: *Microextraction, Sample preparation, Volatile organic compounds, Wood-based Panels*

Wood-based panels (WBP) are wood products made from particles or fibres glued together with an adhesive that is consolidated in a hot plate press, forming a solid panel. The most common WBP are particleboard (PB), dry-process fibreboard (MDF), plywood (PW) and oriented strand board (OSB). These products have become widely used in construction, furniture and for decorative purposes, and are, nowadays, considered a relevant source of contamination to the indoor air quality, due to the emission of volatile organic compounds (VOC). The emission of VOCs can result from the raw materials, chemical additives, or processes used during panel production [1]. One of the most relevant VOC, formaldehyde, was classified by the International Agency for Research on Cancer (IARC) as a group 1 human carcinogen.

In recent years, we have been focusing on developing simple and sustainable sample preparation strategies for the determination of VOC emitted from WBP.

Gas-diffusion microextraction (GDME) is an innovative sample preparation technique for volatile compounds, developed and patented in our research group [2]. The extraction process is based on the volatile compounds transfer from the sample through a gas-permeable membrane into a liquid acceptor phase. GDME can be combined with labelling (or derivatization) to improve separation and/or detection of the analytes. Overall minimal sample manipulation is required and a clean extract relatively free of interfering compounds can be attained. GDME has previously been used for the analysis of important quality markers in different liquid and solid samples [3] and, recently, it was successfully applied to the determination of VOC in different WBP [4,5]. Another approach that has been explored, relies on the dynamic sorption of volatile analytes into commercially available solid phase extraction (SPE) cartridges using a stream of N_2.

In this work, the application of these methods to the determination of VOC in WBP is presented, together with the evaluation of the different emission profiles observed among WBP with different characteristics.

Acknowledgements
This work received financial support from national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through project PTDC/CTM-PAM/1348/2021 (DOI 10.54499/PTDC/CTM-PAM/1348/2021).

This work received support and help from FCT/MCTES (LA/P/0008/2020 DOI 10.54499/LA/P/0008/2020, UIDP/50006/2020 DOI 10.54499/UIDP/50006/2020 and UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020) through national funds. J. R. Santos acknowledges the funding program (DL 57/2016 – Norma transitória, ref. SFRH/BPD/76544/2011) supported by FCT. RMR acknowledges FCT for the Junior Research fellowship CEECIND/04259/2017 through the Individual Call to Scientific Employment Stimulus.

References

[1] T. Adamová, J. Hradecký, M. Pánek, Volatile Organic Compounds (VOCs) from Wood and Wood-Based Panels: Methods for Evaluation, Potential Health Risks, and Mitigation, Polymers 12 (2020) 2289.
[2] G. Pacheco, I. M. Valente, L. M. Gonçalves, J. A. Rodrigues, A. A. Barros, Gas-diffusion microextraction, J. Sep. Sci. 33 (2010) 3207-3212.
[3] P. F. Brandão, R. M. Ramos, P. J. Almeida, J. A. Rodrigues, Determination of Carbonyl Compounds in Cork Agglomerates by GDME-HPLC-UV: Identification of the Extracted Compounds by HPLC-MS/MS, J. Agr. Food Chem. 65 (2017) 1037-1042.
[4] F. D. Gonçalves, M. L. Almeida, J. M. Martins, L. H. Carvalho, J. A. Rodrigues, R. M. Ramos, Gas-diffusion microextraction combined with HPLC-DAD for the comprehensive analysis of volatile carbonyl compounds in wood-based panels, Talanta 272 (2024) 125818.
[5] F. D. Gonçalves, J. M. Martins, L. H. Carvalho, J. A. Rodrigues, R. M. Ramos, Volatile carbonyl compounds emission in dry-process fibreboard: Identification through a selective GDME-HPLC-DAD-MS/MS method, Separations 11 (2024) 92.

Biomass Cooking and Air Quality: A Study on Volatile Organic Compounds via Thermal Desorption GC-MS

O-23

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Keywords*: Firewood combustion, Household air pollution, Non-target screening, Sustainable cooking solutions, Thermal desorption gas chromatography – mass spectrometry (TD GC-MS), Volatile organic compounds (VOCs)*

Cooking with wood biomass fuels on traditional three-stone open fires releases hazardous air pollutants, including volatile organic compounds (VOCs), that often disproportionally affect women and children. This study, conducted in Kwale and Siaya counties in Kenya, employed thermal desorption gas chromatography – mass spectrometry to analyse VOC emissions from cooking with a wood biomass three-stone open fire vs. top-lit updraft gasifier stove. In kitchens with adequate ventilation, total VOC levels increased from 39-285 µg·m^{-3} before cooking to 2224-5406 µg·m^{-3} during open fire cooking, whereas use of a gasifier stove reduced emissions from cooking by 49-78% (497-2741 µg·m^{-3}). However, in kitchens with poor ventilation, there was only a moderate difference in total VOC levels between the two methods of cooking (8954-9295 µg·m^{-3} vs. 7693-8080 µg·m^{-3} for the three-stone open fire vs. gasifier stove, respectively). Using a non-target screening approach to analyse different VOC classes, significantly increased levels of benzenoid, oxygenated and heterocyclic compounds were detected when cooking with the traditional open fire, especially in closed kitchens, highlighting the effects of poor ventilation. Key hazardous VOCs included benzene, naphthalene, phenols and furans, suggesting potential health risks from cooking. In kitchens with good ventilation, use of the gasifier stove markedly reduced emissions of these priority toxic VOCs compared to cooking with an open fire. Thus, substituting open fires with gasifier stoves could help to improve household air quality and alleviate health risks. The study revealed that VOCs were present prior to cooking, possibly originating from previously cooked food (buildup) or the outside environment and were also exacerbated by reduced air flow in high humidity during rainfall, suggesting areas for further research. The findings underscore the importance of adopting cleaner cooking technologies and enhancing kitchen ventilation to mitigate the impacts of VOCs in developing countries.

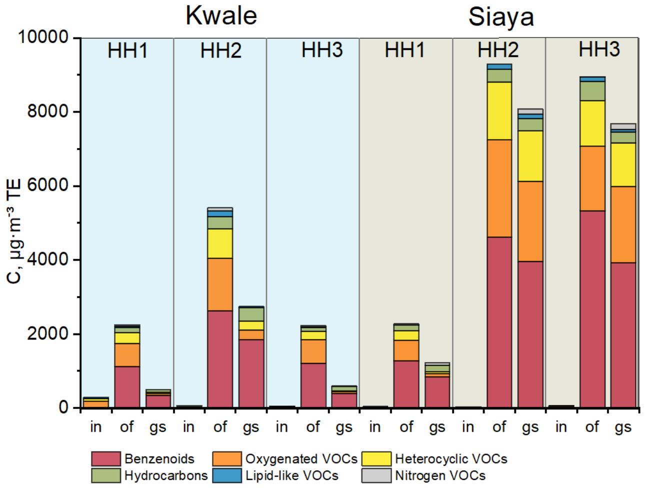

Figure 1. VOC levels (y axis; expressed as µg·m^{-3} toluene equivalents) in kitchen air samples (x axis). Abbreviations: HH – household; in – initial (before cooking); of – three-stone open fire; gs – gasifier stove.

Acknowledgements

This work was supported by the Swedish Research Council for Sustainable Development, Formas [grant 2019-00458].

On the Determination of the Photodegradation Extent of Microplastics: Lights and Shadows of Micro-FTIR Spectroscopy

O-24

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Keywords: *Micro-FTIR spectroscopy, Microplastics, Photodegradation, Principal component analysis*

Understanding the origins of microplastics and evaluating the consequences of plastic pollution hinges upon precise chemical information. In this regard, a remarkable challenge lies in the chemical changes that microplastics undergo due to photoaging, which hinder spectroscopic matching and identification [1]. Micro-FTIR is currently one of the go-to techniques for the screening of microplastics, coupling the possibility of collecting optical images of the particles with the chemical information provided by the IR spectra. The sensitivity of reflectance micro-FTIR spectroscopy to the thickness of the particles and to chemical changes induced by photodegradation on one hand hinders the automated recognition by spectral matching [2], but on the other hand contains layers of information that lie beyond the reaching of conventional data analysis. In this study, we aim to develop a method for the identification and the determination of the degree of photo-oxidation of microplastics, exploiting the multivariate analysis of micro-FTIR data. We studied four types of microplastics obtained by common objects: two conventional (PE and PS) and two compostable bioplastics (PLA and PBAT). which underwent artificially accelerated photoaging and were analyzed by micro-FTIR spectroscopy in the medium infrared range. Principal component analysis (PCA) was able to classify the polymers and show degradation trends, highlighting even subtle changes in the spectra. Particular attention was given to the preprocessing of the dataset, which proved to be essential and has great impact on the outcome of the analysis. Different preprocessing steps were therefore tested and evaluated. The issue of reflection spectral "artifacts" obtained from particles thicker than 100 μm, which often hinder the recognition of the polymer by spectral matching, was also addressed. The aim is to develop a robust analysis method that can be coupled with automated mapping.

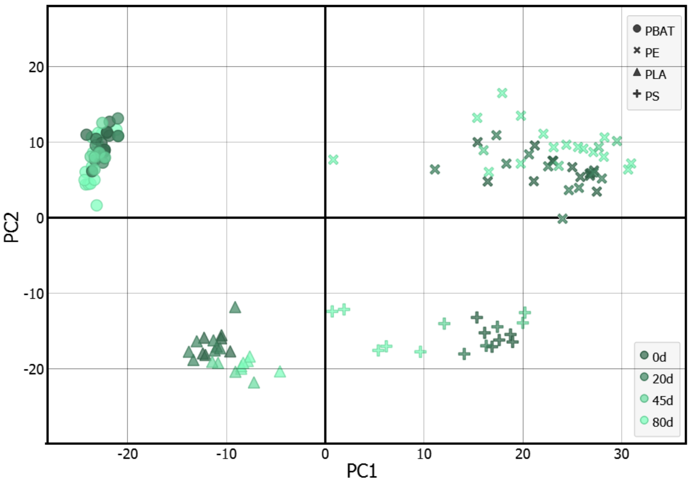

Figure 1. PCA scores plot of the four types of microplastics at different aging.

References

[1] C. Rathore, M. Saha, P. Gupta, M. Kumar, A. Naik, J. De Boer, Standardization of micro-FTIR methods and applicability for the detection and identification of microplastics in environmental matrices, Sci. Total Environ. 888 (2023) 164157

[2] J.-L. Xu, K. V. Thomas, Z. Luo, A. A. Gowen, FTIR and Raman imaging for microplastics analysis: State of the art, challenges and prospects, TrAC Trends Anal. Chem.119 (2019)115629.

X-ray Fluorescence-Based Studies of Particulate Matter on Filter

O-25

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Keywords: *Elemental quantification, Particulate matter, Reference material, Toxic elements, X-ray fluorescence analysis*

X-ray Fluorescence (XRF), despite its appealing capabilities, is still considered behind on the list of analytical techniques to be employed for the elemental characterization of matter. XRF-based techniques are presenting however, interesting advantages. One of these, and not the least, is that XRF is usually regarded as a green, sustainable analytical technique. It is mostly non-destructive, requires fewer chemicals and generates less or no waste, in comparison to other wet analytical methods. In addition, XRF allows analysts, in some cases, for direct analysis of their samples, without or with little sample preparation and handling. Commercial XRF spectrometers are typically compact, and may be used directly at-line or off-line the sampling site, with both instruments and operations being cost-effective. As such, XRF techniques are presenting some interesting alternatives to primary methods such as Atomic Absorption (AAS) or Inductively Coupled Plasma (ICPs) based spectrometries, which rely on tedious sample preparation procedures and potentially suffer from low recovery rates.

XRF can be widely used for simultaneous elemental and chemical analysis as once sorted, the intensity of each characteristic emission is proportional to the amount of the corresponding element present in the given material. Total Reflection X-ray Fluorescence (TXRF), as an example, enables experimentalists to simultaneous determine the elemental compositions with detection limits in the low picogram range, and even lower if a synchrotron is used as X-ray source.

Particulate matter (PM) is among the six primary environmental pollutants, and its associated health and environmental risks well established. The situation is critical, with less than 30% of the global population exposed to PM$_{2.5}$ levels below the threshold recommended by the World Health Organization (WHO), with additional PM monitoring, characterization and controls needed. In Europe, the Clean Air Policy (Directive 2004/107/EC) has determined the thresholds for potentially toxic elements as Pb, Cd, As. Ni and Hg, the environmental agencies must control.

PMs are traditionally collected onto filtering membranes (filters), and their mass amounts and composition determined. As previously mentioned, XRF techniques (e.g., TXRF) present interesting and more sustainable alternative to reference techniques AAS or ICPs, giving comparable results and probing the filters directly without the need to digest them. PM filters can also be prepared with the Smart Store® method, which encloses the collected filters between two polymeric layers. This process avoids material losses, contaminations, and allows the sample to be preserved. Used with a TXRF spectrometer, the method has been shown to be suitable for the elemental quantification of PMs [1]. To determine the PMs' elements of interests, such as Class 1 human toxicants (Pb, Hg, As, Cd), environmental scientists need reliable and accurate elemental analysis techniques underpinned by calibration procedures employing fit-for-purpose reference materials (RM). Unfortunately, RM representative of PM filters are crucially lacking, with no adequate concentration ranges for PMs covering the targeted applications. These analyses include environmental and health monitoring, air quality, workplace and stationary emission sources, for instance. The few reference materials for PMs known (i.e., NIST CRM 2783, NIST 2783 Polycarbonate membrane with known deposited amount of unban PM2.5, NIST RM 8786 PM2.5 SRM 1649a Urban Dust resuspended in air and filtered onto quartz-fiber filter, and CRM SL-MR-2-PSF-01 PM10 deposited on quartz filter, some of which non-longer available), only emphasize the lack of representativeness and suitability of these RMs for the various applications targeted.

A COST Innovator Grant (CIG) 18130, "AIR particulate reference material for elemental quantification and CALibration procedures", acronym AIR-CAL [2], arose out of these crucial needs for RMs. This venture is focusing on the developments of RMs for the characterization of PMs from the technological, normative, application and commercial points of view.

Here, we present data from a set of calibration samples realized by nebulizing a solution of a reference material with a particle generator and collecting the obtained aerosols onto a filter. By varying the nebulization time and changing the concentration of the solution, filters loaded with a wide range of elemental masses may be obtained. Filters were then prepared according to the Smart Store® method and characterized with XRF under grazing incidence conditions. We compared these results with solutions, with the same composition, deposited as droplets onto a carrier and characterized using TXRF. Formally, the nebulized residues on the filters prepared with the Smart Store® do not satisfy the conditions underpinning quantitative TXRF, but we demonstrate that the retrieved net intensities may be used to build an external calibration curve, and allow for quantification procedures for PMs captured on air filters at environmentally relevant levels.

Acknowledgements
This abstract is based upon work from COST Action CA18130 and from the COST Innovator Grant IG18130 supported by COST (European Cooperation in Science and Technology), www.cost.eu.

References

[1] P. Cirelli F. Bilo, K. Tsuji, T. Matsuyama, G. Siviero, L. Pisani, A. Zacco, L.E. Depero, D. Eichert, L. Borgese, Assessment of calibration methods for Pb-loaded aerosol filters analysed with X-ray fluorescence under grazing incidence, Spectrochim. Acta Part B At. 192 (2022) 106414.
[2] https://enforcetxrf.eu/ig18130/; https://www.cost.eu/actions/IG18130/.

3D-Printed Millifluidic Extraction Devices Encompassing Solid and Liquid Biopolymeric Phases

O-26

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Keywords: *Biopolymeric materials, Environmental analysis, Flow analysis, Membrane extraction*

Environmental analysis is challenging due to the inherent characteristics of the samples, the heterogeneity (spatial and temporal) together with their complexity. The low concentration of the compounds of interest in these samples together with the large amount of compounds present make the use of new analytical methodologies necessary [1]. It should be underlined that the sampling and the sample preparation stages are crucial for reliable analysis. To simplify the sample preparation step, flow-through analytical devices and 3D printed devices have been developed so as to increase the degree of automation of the methodology and foster method optimization [2].

In this line, new extraction materials (solvents and sorbents) have been proposed to be amenable to these flow-through systems. The simplest methodologies are based on the preparation of planar sorptive phases, consisting of the functionalization of a substrate. Supports described in the literature include metal foils [3] and polymers [4], such as biopolymers or 3D-printed stereolithographic supports, just to mention a few. Both options are currently being exploited in many labs on account of their availability, cost and ease of chemical functionalization. Moreover, biopolymeric solvents, such as natural deep eutectic solvents [5] can be also combined with 3D printed planar structures for advanced sample preparation in the field of sustainable development goals and circular economy, as discussed in this presentation.

Acknowledgements

FAC-C, EJC-C, and MM acknowledge the financial support from the Spanish State Research Agency (Agencia Estatal de Investigación, AEI/10.13039/501100011033), the Spanish Ministry of Science and Innovation (Ministerio de Ciencia e Innovación, MCIN) and the European Union (NextGenerationEU/PRTR) through projects PID2020-117686RB-C33 (AEI/MCIN) and TED2021-131303B–I00 (MCIN/AEI/NextGenerationEU/PRTR). JM-S, RL, and SC acknowledge the financial support from the Andalusian counseling of “Transformación Económica, Industria, Conocimiento y Universidades” (PY20_00461). The authors extend their appreciation to MCIN for granting the Spanish Network of Excellence in Sustainable Sample Preparation (RED2022-134079-T).

References

[1] F.A. Casado-Carmona, G. Lasarte-Aragonés, R. Lucena, S. Cárdenas, Green sample preparation techniques in environmental analysis, Green Approaches Chem. Anal. (2023) 241–276.

[2] D.J. Cocovi-Solberg, P.J. Worsfold, M. Miró, Opportunities for 3D printed millifluidic platforms incorporating on-line sample handling and separation, TrAC Trends Anal. Chem. 108 (2018) 13–22.

[3] C. Calero-Cañuelo, F.A. Casado-Carmona, R. Lucena, S. Cárdenas, Mixed-mode cationic exchange sorptive tapes combined with direct infusion mass spectrometry for determining opioids in saliva samples, J. Chromatogr. A. 1702 (2023) 464097.

[4] M. González-Bermúdez, Á.I. López-Lorente, R. Lucena, S. Cárdenas, Paper-based sorptive phases for a sustainable sample preparation, Adv. Sample Prep. 5 (2023) 100051.

[5] I. López-Ruiz, G. Lasarte-Aragonés, R. Lucena, S. Cárdenas, Deep eutectic solvent coated paper: Sustainable sorptive phase for sample preparation, J. Chromatogr. A. 1698 (2023) 464003.

Metal Nanoparticles Laser Writing on Cellulosic Substrates for Affordable Colorimetric Paper-Based Analytical Device Development

O-27

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Keywords: *Catalytic paper, Colorimetric devices, Laser-induced metal nanoparticles, Plasmonic paper, Photoluminescent paper*

Nowadays, the manufacturing of easy-to-use and sustainable point-of-need devices is a hot topic. In this framework, the colorimetric approaches, which employ optical variation easily monitorable by naked eye or smartphone, can offer captivating opportunities. Due to its high availability, 3D structure, capillarity, mechanical resistance, flexibility, and biodegradability, the paper represents an excellent substrate for the fabrication of paper-based analytical devices (PAD). Paper's color, porosity, and intrinsic chemical features, make it a straightforward building block for developing colorimetric PAD, allowing also the anchoring/storing of sensing materials and reagents, and the realization of microfluidics set-up. Among sensing materials, metal nanoparticles (MNP) are useful colorimetric probes/tags due to their peculiar chemistry and optical features (i.e., localized surface plasmon resonance/ LSPR, and luminescence). Properly synthesized MNP returns visible colors offering infinite opportunities for developing optical and colorimetric PAD; however, paper decoration with MNP with high resolution and defined patterns is still a challenge.

In this presentation, a CO_2-laser plotter-based innovative and versatile strategy to synthesize on paper plasmonic active gold (Au), silver (Ag), platinum (Pt), copper (Cu), cerium (Ce), nickel (Ni), and aluminum (Al) nanostructures will be presented [1]; this approach allows to form metal-nanostructures on different paper substrates including Whatman paper, office paper, recycled office paper, rice paper, etc. The laser-induced metal nanoparticles (LIMs) result well anchored onto paper, allowing on-demand designs. LIMs possess analytical useful features i.e., (i) are plasmonic active, (ii) possess catalytic features and (iii) show photoluminescent; these features are related to the LIM chemistry and morphology. Therefore, LIMs have been integrated into different lab-made PADs coupled with smartphone-based readouts. The proposed PADs were conceived to integrate analysis steps and facilitate result-readout and were manufactured using low-cost benchtop technologies (i.e., laser/cutter-plotter, thermal-laminator, etc.) and office-grade substrates (i.e., polymeric-sheets, cellulosic substrates, etc.).

In this presentation will be presented different PADs enclosing LIMs. (**i**) A treble lateral-flow device (LF^3) for direct milk analysis aimed at the determination of sodium hypochlorite related to bleaching frauds will be shown. The LF^3 is equipped with Ag, Au, and Ce-LIMs that act as colorimetric tags enabling different levels of contamination evaluation; the sensing strategy relies on the analyte-mediated LIM etching resulting in paper-substrate discoloration. The LF^3 is designed to work directly with milk exploiting the paper fluidics to filter/clean the samples. (**ii**) A flip paper-based device (Flip-PAD) for the selective determination of ascorbic acid in food and supplements will be presented. The Flip-PAD exploits Pt-LIM oxidase-like activity to obtain a dye-based colorimetric readout, without needing external reagents and allows to obtain accurate analytical results in 1 minute. (**iii**) Eventually, a fluorometric PAD for the selective detection of o-diphenols in food samples will be also presented. In this case, the Al-LIM fluorescence turn-on is exploited for the detection of the analytes. Interestingly, this PAD allows obtaining qualitative and quantitative results thanks to the LIM's unique features.

Summing up, the proposed laser writing strategy can be considered a new sustainable nanopatterning technique, particularly prone to generate optical sensing zones useful to fabricate within everyone's reach paper-based colorimetric devices, conceived to solve analytical issues reducing the use of chemicals and solvents.

Acknowledgments

This research was funded by the European Union – Next Generation EU. Project Code: ECS00000041; Project CUP: C43C22000380007; Project Title: Innovation, digitalization and sustainability for the diffused economy in Central Italy – VITALITY

References

[1] A. Scroccarello, F. Della Pelle, T. Di Giulio, E. Mazzotta, C. Malitesta, D. Compagnone, Single-Stroke Metal Nanoparticle Laser Scribing on Cellulosic Substrates for Colorimetric Paper-Based Device Development. ACS Sustainable Chemistry & Engineering. 12(8) (2024) 3196–3208.

A Composite Hydrogel Beads for Vortex-Assisted Dispersive Micro-Solid Phase Extraction of Food Additives Followed by HPLC-DAD

O-28

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Keywords: *Food additives, High-performance liquid chromatography, Hydrogel beads, Vortex-assisted dispersive micro-solid phase extraction*

A composite alginate hydrogel beads sorbent was fabricated for vortex-assisted dispersive micro-solid phase extraction and preconcentration of parabens and synthetic phenolic antioxidants from selected foodstuffs. The composite sorbent consists of a covalent organic framework incorporated into alginate hydrogel beads. It could adsorb parabens and synthetic phenolic antioxidants via hydrogen bonding, hydrophobic, and π-π interactions. The fabricated sorbent was characterized, and extraction conditions were optimized. High-performance liquid chromatography with a diode array detector was utilized to separate and quantify extracted food additives. Under optimum conditions, linearity was in the range of 1.00 to 100 μg kg^{-1} for methyl parabens and 2.00 to 100 μg kg^{-1} for tertiary butylhydroquinone, propyl parabens, butyl parabens, and butylated hydroxyanisole. Limits of detection ranged from 0.25 to 0.50 μg kg^{-1}. The developed composite sorbent was successfully applied to extract and determine parabens and synthetic phenolic antioxidants in tomato paste, mayonnaise, infant milk powder, and coffee creamer samples. Recoveries ranged from 89 to 99% with RSDs lower than 7%. The vortex-assisted extraction approach was convenient, and the fabricated sorbent could be reused for up to 8 extraction-desorption cycles.

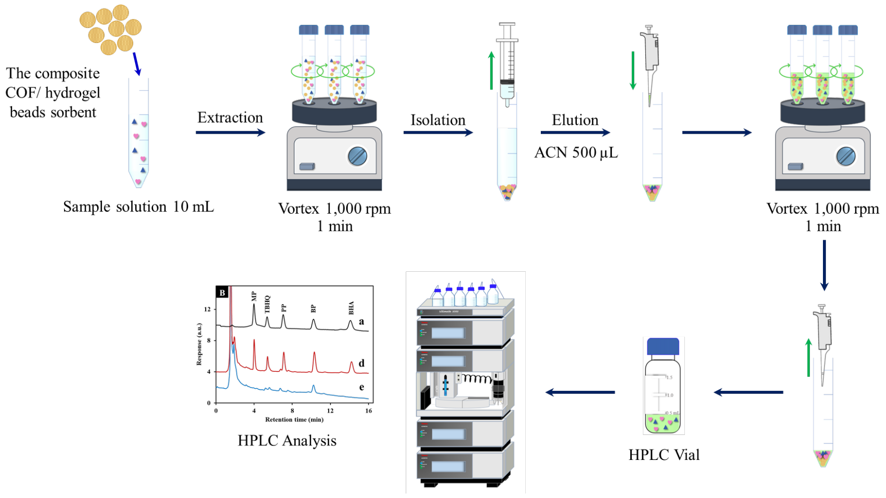

Figure 1. Vortex-assisted dispersive micro-solid phase extraction of food additives followed by high performance liquid chromatography analysis.

Effects of Different Extraction Methods on Antioxidant Properties of Seaweeds

O-29

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Keywords: *Central Composite design, Subcritical-water extraction, Total phenolic content, Ultrasonic-assisted extraction, Water extraction*

Seaweeds (red, brown, and green) contain a plethora of biologically active substances, including a variety of natural antioxidant compounds [1]. In addition, the antioxidant extracts and compounds from seaweeds may have applications in prolonging the shelf life of food products by retarding oxidation and peroxidation processes [2].

Effective extraction and proper assessment of antioxidants from seaweeds are crucial to exploring potential antioxidant sources and promoting their application.

Several methods using water as a solvent have been employed to enhance the extraction efficiency of antioxidant components from seaweeds. The antioxidative properties of four brown seaweeds (*Eisenia bicyclis, Fucus vesiculosus, Himanthalia elongata, Undaria pinnatifida*), four red seaweeds *(Chondrus crispus, Gracilaria gracilis, Palmaria palmata, Porphyra dioica*) and two green seaweeds (*Codium tomentosum, Ulva lactuca*), extracted using different methods, were compared, and analyzed. Three extraction methods were performed: conventional water extraction, Ultrasound-Assisted Extraction (UAE), and Subcritical-Water Extraction (SWE).

The water extraction was performed at three different temperatures (25 ºC, 50 ºC, and 75ºC); four different rations (1:100, 1:75, 1:50, 1:25); and three different durations (1 h, 3 h, and 5 h). Total phenolic content (TPC) was determined for individual extracts using the Folin–Ciocalteu method [3]. The obtained results were analyzed using the "Design Expert 11" software to generate two matrices, "Central Composite Design" (CC) and "Box-Behnken," (BB) aimed at identifying the optimum extraction conditions (temperature, time, and ratio) for each seaweed. The optimum parameters identified from each design were experimentally verified.

The optimal ratio determined from the water extraction was applied to both (i) the UAE method, using a high-speed ultrasonic homogenizer (VCX 750-Watt Ultrasonic Processor, 220, SONICS & MATERIALS, Newtown, USA), and (ii) the Subcritical Water Extraction (SWE) method, employing a Parr Series Mini Bench Top Reactor 4568 connected to the Parr 4848 Reactor Controller (Moline, IL, USA). The ultrasonic extraction was evaluated at two durations, 10 minutes, and 20 minutes, while SWE was tested at 140°C with 30 bar pressure and 190°C with 40 bar pressure.

The CC design demonstrated a better fit than the BB for all seaweeds except for *P. dioica*. For the CC design, the TPC predicted values ranged from 1.100 mg GAE/g (*P. palmata*) to 34.10 mg GAE/g (*F. vesiculosus*). Following the optimum parameters obtained by experimental design, experimental TPC values varied from 1.169 mg GAE/g (*P. dioica*) to 31.80 mg GAE/g (*F. vesiculosus*). The TPC data from the UAE and SWE extracts indicated that these methods effectively extract valuable bioactive compounds, exhibiting higher TPC values for all tested seaweeds.

The results revealed that commercially processed seaweeds exhibit various antioxidant properties. Notably, these findings highlight the promising potential of utilizing scalable and environmentally friendly extraction methods in the food industry, such as the UAE and SWE. These greener extraction techniques offer a sustainable alternative to conventional methods and facilitate the development of functional foods enriched with natural antioxidants to improve consumers' well-being.

Acknowledgements

This work received support and help from FCT/MCTES (LA/P/0008/2020 DOI 10.54499/LA/P/0008/2020, UIDP/50006/2020 DOI 10.54499/UIDP/50006/2020 and UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020) financed by FCT/Ministério da Ciência, Tecnologia e Ensino Superior (MCTES) through national funds. This work has been developed within the scope of the “BLUE BIOECONOMY INNOVATION PACT” (Project Nº C644915664-00000026), financed by NextGenerationEU, under the incentive line “Agendas for Business Innovation” of the Recovery and Resilience Plan (RRP).

PACTO DA BIOECONOMIA AZUL
PRR Plano de Recuperação e Resiliência
REPÚBLICA PORTUGUESA
Financiado pela União Europeia NextGenerationEU

References

[1] I. Guerreiro, R. Magalhães, F. Coutinho, A. Couto, S. Sousa, C. Delerue-Matos, V. F. Domingues, A. Oliva-Teles, H. Peres. Evaluation of the seaweeds Chondrus crispus and Ulva lactuca as functional ingredients in gilthead seabream (Sparus aurata), Journal of Applied Phycology 31(3) (2019) 2115–2124.

[2] L.L. Pruteanu, D.S. Bailey, A.C. Grădinaru, L. Jäntschi, The Biochemistry and Effectiveness of Antioxidants in Food, Fruits, and Marine Algae. Antioxidants, Antioxidants. 12(4) (2023) 860.

[3] Barroso, M. Fátima, et al. "Total antioxidant capacity of plant infusions: Assessment using electrochemical DNA-based biosensor and spectrophotometric methods." Food control 68 (2016): 153-161.

Dynamic Headspace Vacuum In-Tube Extraction and GC-MS for Analyzing Volatile Compounds in Various Matrices

O-30

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Keywords: *DHS-VTT, GC-MS, Matrix, Volatiles*

The analysis of samples with strong matrices often presents challenges during sample preparation and analysis, particularly in the determination of volatile compounds using gas chromatography-mass spectrometry (GC-MS). Usually, one tries to separate the matrix from the sample, which often are elaborate procedures. In many cases, headspace analysis alone is not sensitive or sufficient. Therefore, microextraction methods such as solid-phase microextraction (SPME) [1] and in-tube extraction (ITEX) [2] have gained attention in the last decades. These techniques show additional advantages such as automatability, sustainability, easy application and no solvent consumption. In complex matrices, the concentrations of different compounds can vary widely, which is a problem when using SPME because the phase volume is small and saturates quickly. ITEX techniques have a much larger phase volume and achieve higher enrichment factors when the sample headspace is sucked through the sorbent material several times. However, it has been found that the performance of headspace techniques is improved under reduced pressure, as demonstrated by vacuum SPME techniques [3]. We present here a technique in which classical ITEX was applied under vacuum, called Dynamic Headspace Vacuum In-Tube Extraction (V-ITEX, based on the DHS-VTT technique [4]), which was compared with classical ITEX and SPME and applied to several different matrices. In addition, a simple modification of the autosampler was carried out in order to apply V-ITEX automatically. The extraction of volatiles by V-ITEX is fast, shows low artefact formation and a higher evaporation rate of the compounds. Compared to classical techniques, V-ITEX is more time efficient and more sensitive. The higher extraction efficiency allows the analysis of smaller sample volumes, the use of split systems with two or more detectors or integration into olfactometric analyses. In conclusion, the V-ITEX technique is very promising for the field of volatile analysis.

References

[1] C. L. Arthur, J. Pawliszyn, Solid phase microextraction with thermal desorption using fused silica optical fibers, Anal. Chem. 62 (1990) 2145-2148.
[2] M. A. Jochmann X. Juan, B. Schilling, T. C. Schmidt In-tube extraction for enrichment of volatile organic hydrocarbons from aqueous samples, J. Chromatogr. A 1179 (2008) 96-105.
[3] N. P. Brunton, D. A. Cronin, F. J. Monahan, The effects of temperature and pressure on the performance of carboxen/PDMS fibres during solid phase microextraction (SPME) of headspace volatiles from cooked and raw turkey breast, Flavour Fragr. J. 16 (2001) 294-302.
[4] P. Fuchsmann, M. T. Stern, P. Bischoff, R. Badertscher, K. Breme, B. Walther, Development and performance evaluation of a novel dynamic headspace vacuum transfer "In Trap" extraction method for volatile compounds and comparison with headspace solid-phase microextraction and headspace in-tube extraction, J. Chromatogr. A 1601 (2019) 60-70.

Breaking Barriers with Automation: Automated Vac-HS-SPME for Enhanced Detection and Workflow Efficiency

O-31

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***Keywords:** Automation, Food matrices, Solid Phase Micro Extraction (SPME), Vacuum-assisted*

Headspace Solid Phase Microextraction (HS-SPME) is a well-established technique for determining volatiles by gas chromatography in various matrices and applications. However, due to analyte mass transfer being a rate-limiting step in the process, HS-SPME is intrinsically more effective in extracting volatile rather than semi-volatile analytes. Further, to facilitate the extraction of semi-volatile analytes, HS-SPME methods often require long extraction times and high extraction temperatures to speed up the kinetics of analyte transfer to the headspace [1]. However, this approach introduces the risk of sample decomposition or the creation of new compounds, such as with the Maillard reaction in food matrices, giving rise to artefacts within the chromatographic data. Recently, an additional parameter has been proposed to overcome this limitation: the application of vacuum [2]. Applying vacuum during HS-SPME has been shown to improve extraction kinetics for some semi-volatile sample components, resulting in higher extraction efficiencies and analyte sensitivity, with shorter sampling times and at milder sampling temperatures [3].

To date, Vacuum-Assisted HS-SPME (Vac-HS-SPME) approaches have been carried out by applying the vacuum manually, offline, and then analysing the samples on the HS-SPME-GC platform. Automating this step will benefit the operator significantly, including speed, throughput, and the ability to run the system unattended. The evacuation can be added as part of the automated analysis method with no analyst ‘touch time’ involved. This work describes the development of a fully automated approach for Vac-HS-SPME using the existing GERSTEL hardware and software [4]. The workflow has been proven to be robust and reproducible. A custom-made suitability test mixture has been compiled to assess the system's performance regularly. The automated platform also includes a dedicated cooled tray for 20mL headspace vials and a cooled agitator to allow seamless and reliable testing of samples at sub-ambient temperatures, taking advantage of the enhanced efficiency of the vacuum-assisted SPME analysis. To showcase the added value offered by this workflow for food applications, untargeted and targeted analysis of a variety of dairy and dairy-free products was performed, with a specific focus on the detection of lactones such as δ-decalactone (δ-C10), δ-dodecalactone (δ-C12), δ-tetradecalactone (δ-C14), whose presence is associated with the desired buttery flavour in dairy fat [5].

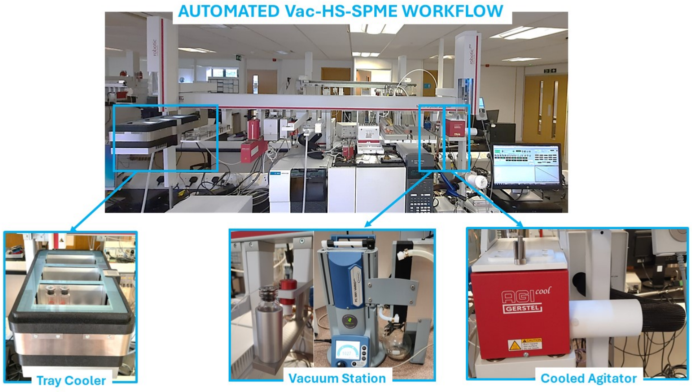

Figure 1. Automated Vac-HS-SPME workflow

References

[1] C.Lancioni, C.Castells, R.Candal, M. Tascon, Headspace solid-phase microextraction: Fundamentals and recent advances, Advances in Sample Preparation 3 (2022) 100035

[2] E. Psillakis, E. Yiantzi, L. Sanchez-Prado, N. Kalogerakis, Vacuum-assisted headspace solid-phase microextraction: Improved extraction of semivolatile by non-equilibrium headspace sampling under reduced pressure conditions Anal. Chim. Acta 742 (2012) 30.

[3] N. Delbecque, S. Mascrez, E. Psillakis, G. Purcaro, Sub-ambient temperature sampling of fish volatiles using vacuum-assisted headspace solid-phase microextraction: Theoretical considerations and proof of concept, Anal. Chim. Acta 1192 (2022) 339365.

[4]https://content.yudu.com/web/14zjy/0A1wpyz/LMUK49.3/html/index.html?refUrl=https%253A%252F%252Fwww.labmate-online.com%252F&page=6

[5] H. Zia, U. Von Ah, Y.H. Meng, R. Schmidt, J. Kerler, P. Fuchsmann, Biotechnological formation of dairy flavour inducing δ-lactones from vegetable oil, Food Chemistry 13 (2022) 100220.

Microextraction Strategies for Lipid Peroxidation Analysis in Infant Formulae

O-32

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Keywords: *DLLME, GDME, Infant formulae, Lipid peroxidation, SPME*

Infant formulae are the only food products recommended by the World Health Organization (WHO) complementary or alternately to breastfeeding [1]. Therefore, determining lipid peroxidation products in infant formulae is crucial to maintain their nutritional quality and safety, meeting infants' dietary needs while minimizing health risks from oxidative degradation. Lipid peroxidation is a significant concern in food systems, producing reactive organic compounds that affect sensory qualities and consumer health [1-3]. While controlled lipid peroxidation can enhance the flavors and appearance of certain foods, the emergence of secondary peroxidation products often leads to sensory degradation and undesirable flavors in various products, including oils, alcoholic and non-alcoholic beverages, infant food, and plant-based food items, among others [1-3]. Concerns arise regarding secondary peroxidation products like acrolein, acrylamide, malondialdehyde and other carbonyl compounds, which may pose toxic and mutagenic risks by interacting with biomolecules [1-2]. The International Agency for Research on Cancer (IARC) has classified these compounds for their carcinogenic hazards, while the European Food Safety Authority (EFSA) has set daily intake limits. Further investigation into their occurrence and toxicity is necessary to develop mitigation strategies for food quality and safety [1-3].

Traditional analytical methods like the TBARS assay lack specificity and require complex analysis steps. Novel derivatization reagents such as phenyl hydrazine and its derivatives, especially in combination with LC/GC-MS, offer improved sensitivity and specificity for lipid peroxidation analysis [1-3]. Sample preparation plays a pivotal role in the analysis process, with traditional approaches frequently involving extensive solvent use and multiple steps, leading to significant waste generation and time consumption. In response to these challenges, microextraction techniques, including dispersive liquid-liquid microextraction (DLLME), solid-phase microextraction (SPME), and gas-diffusion microextraction (GDME), have emerged as promising alternatives [2-4]. These techniques utilize minimal amounts of extracting phase relative to the sample volume, reducing solvent usage and facilitating analyte pre-concentration, in line with current trends in *Green Analytical Chemistry*. The selection of a microextraction method depends on various factors, including the sample's state, instrumental method of analysis, and properties of the analyte.

The recent applications of microextraction techniques in lipid peroxidation product analysis are presented here. These techniques provide efficient and sensitive approaches to extract and quantify lipid oxidation products in infant formulae, thereby enhancing our comprehension of oxidative deterioration. This communication includes discussions on recent advancements, challenges, and limitations, with a focus on emphasizing the potential for ongoing innovation and improvement in infant formulae analysis.

Figure 1. General scheme of microextraction techniques used in lipid peroxidation products determination.

Acknowledgements
The research is supported by the Polish National Science Center within the project 2021/43/D/NZ9/01572 as part of the SONATA program, and withing the project 2023/07/X/NZ9/01113 as part of the MINIATURA-7 program.

References

[1] Maldonado-Pereira, L., et al. Dietary exposure assessment of infant formula and baby foods' oxidized lipids in the US population. Food Chem. Toxicol., 172 (2023) 113552.

[2] Custodio-Mendoza, J. A., et al. Innovative Solutions for Food Analysis: Microextraction Techniques in Lipid Peroxidation Product Detection. Separations, 10 (2023) 531.

[3] Custodio-Mendoza, J. A., et al. Green infant formula analysis: Optimizing headspace solid-phase microextraction of carbonyl compounds associated with lipid peroxidation using GC-MS and pentafluorophenylhydrazine derivatization. Talanta 273 (2024) 125816.

[4] Custodio-Mendoza, J. A., et al. (2024). Simultaneous determination of carbonyl compounds related to thermal treatment and oxidative stability of infant formulas by gas-diffusion microextraction and high-performance liquid chromatography with ultraviolet detection. Analytica Chimica Acta, 1288, 342164.

Investigation of Greener Solvents for HPLC

O-33

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Keywords: *Greener chromatography, Greener solvents, HPLC*

High Performance Liquid Chromatography (HPLC) belongs to the analytical techniques that consume the largest volumes of solvents, leading to significant solvent waste. The solvent consumption in HPLC can be reduced by using columns with smaller inner diameter or by using more efficient columns (smaller particle size or superficially porous particles) with shorter column length. All these approaches refer to principle # 5 (miniaturization) of the 12 principles of Green Analytical Chemistry [1].

An approach which is yet not considered too often is addressing principles # 10 (reagents from renewable sources) and # 11 (toxic reagents should be replaced) of Green Analytical Chemistry. This could be achieved by changing to biobased solvents or to solvents with lower toxicity (or ideally a combination of both) than the usual organic modifiers in RP-HPLC such as acetonitrile and methanol.

This work showcases some studies on using ethanol and propylene carbonate as “greener” solvents in HPLC. As ethanol (and especially its mixtures with water) are much more viscous than acetonitrile and methanol, both monolithic silica as well as particle-packed HPLC columns have been employed for this study. Compared to particle packed columns, monolithic columns have some advantages in terms of very low backpressure and improved resistance to matrix due to their high porosity and bimodal pore structure. Data on the influence these greener solvents on separation efficiency, selectivity and backpressure will be discussed. This work will be concluded by different examples applying greener solvents for real-life HPLC applications.

References

[1] A. Gałuszka, Z. Migaszewski, J. Namieśnik, The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices, Trends in Analytical Chemistry 50 (2013) 78–84.

Structural Characterization of Hydrophilic Natural Deep Eutectic Solvents, Evaluation of its Physicochemical Properties and Application to Extract Phenolic Compounds from Tea Samples

O-34

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Keywords: Green sample preparation, Structural characterization, Physicochemical properties, Micro-UAE, NADES

Natural deep eutectic solvents (NADESs) are of particular interest in sample preparation, as they are a promising alternative to the toxic organic solvents used so far. 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 [1]. They present several advantages, such as their biodegradability, low cost, high stability, and low toxicity. Although their applications have increased in recent years, knowledge about their structural characterization and physiochemical properties is still scarce.

In this work, a selection of 14 different hydrophilic NADESs composed of choline chloride, lactic acid, citric acid, glycerol, glucose, fructose and urea were prepared in different ratios using the heating and stirring method. The composition of the NADESs 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:glicerol: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 (1:1:5), choline chloride:glycerol:water (1:2:6), urea:glycerol (1:2), urea:glycerol:water (1:1:2), and urea:lactic acid (1:2). All NADESs were analysed by Nuclear Magnetic Resonance (NMR) spectroscopy to confirm the formation of the supramolecular structure in each case. In particular, nuclear Overhauser enhancement spectroscopy (NOESY) was used to investigate the intermolecular interactions between the corresponding components. After selecting a signal of one of the components by ^{1}H NMR, it was irradiated to see if there were NOE effects in the NOESY spectra meaning a spatial proximity between the components of the NADESs by the formation of hydrogen bonds. This was confirmed in all cases except for urea:lactic (1:2). Afterward, the physicochemical properties of each NADES, such as density, pH, viscosity, refractive index and conductivity, were measured to provide useful information about their potential industrial applications. The values of these properties vary considerably depending on the composition of the NADES.

To test the applicability of the proposed NADESs in sample preparation, they were employed as extraction solvents of phenolic compounds from tea samples. In this regard, the extraction efficiency of each one was evaluated in a micro-ultrasonic assisted extraction (micro-UAE) prior to their determination by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). Thus, 100 mg of dried green tea sample were extracted with 1 mL of each NADES. Then, 100 µL of the supernatant was redisolved in 900 µL water:EtOH (50:50, *v/v*) for injection into the LC-MS/MS system. The best extraction, in terms of the highest signal for the target phenolic compounds, was achieved with the NADES so-called LGLH composed of lactic acid:glycerol:water (1:1:3, molar ratio). Subsequently, the key parameters influencing the micro-UAE were investigated and optimized by response surface methodology (RSM) based on a central composite design (CCD) to reduce the number of experiments and enhance the extraction of the target compounds. Micro-UAE was also evaluated in terms of greenness using the AGREEprep tool and compared with traditional extraction procedures for the extraction of phenolic compounds [2]. In addition, it was observed that the physicochemical properties of the NADES, particularly pH and viscosity, had a great influence on the extraction yields. Thus, extraction of the major phenolic compounds such as catechin compounds was favoured when acid and less viscous NADESs were used.

To sum up, lactic acid, citric acid, choline chloride and urea based NADESs have been characterized in terms of their structural interactions and physiochemical properties. This allows for tailoring NADES according to their future specific application. In addition, micro-UAE using NADESs as extraction solvents has been presented for the first time as a greener alternative for the extraction of phenolic compounds from tea samples.

Acknowledgements

Authors gratefully acknowledge the PPIT-UAL, Junta de Andalucía-FEDER 2021-2027. Programa: 54.A for financial support. LCR thanks "Juan de la Cierva Postdoctoral Scholarship" funded by the Spanish government and Biotectics COR for technical support.

References

[1] A. Paiva, R. Craveiro, I. Aroso, M. Martins, R.L. Reis, A.R.C. Duarte. Natural deep eutectic solvents – solvents for the 21st century. ACS Sustain Chem., 2(5) (2014) 1063-1071.

[2] A.I. López-Lorente, F. Pena-Pereira, S. Pedersen-Bjergaard, V.G. Zuin, S.A. Ozkan, E. Psillakis. The ten principles of green sample preparation. TrAC Trends in Analytical Chemistry. 148 (2022) 116530.

Miniaturized Stir Bar Dispersive Liquid Microextraction (mSBDLME) along with Natural Deep Eutectic Solvent-Based Ferrofluids: A Perfect Match

O-35

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Keywords: *Ferrofluid, Microextraction, Miniaturization, Natural deep eutectic solvents*

The miniaturization of the analytical methods has been gaining great popularity in recent years. Whether it is for the analysis of microvolume samples and/or to reduce the amount of organic solvents and wastes, the developed microextraction techniques must be adapted to this trend.

In this sense, our group has recently achieved the miniaturization of the stir bar sorptive dispersive microextraction (mSBSDME) [1] allowing to treat samples around 100-300 µL besides reducing the amounts of sorbent, organic solvents and wastes.

In the same way, in this communication we propose the miniaturization of its liquid homologous, *i.e.,* the stir bar dispersive liquid microextraction (SBDLME) [2]. Despite at the first look may be seen a simple translation from the same miniaturization process, but using solvents instead of sorbents, the miniaturization of the SBDLME requires deeper research, especially when low-density solvents, such as natural deep eutectic solvents (NADESs), are employed.

The developed miniaturized SBDLME (mSBDLME) presents some benefits compared with the conventional SBDLME and the mSBSDME in terms of simplicity, quickness and waste production that will be detailed in this presentation in addition to its easy combination with NADES and other types of low-density solvents.

In order to show the potential of this new technique, the determination of fentanyl in saliva samples was selected as proof of concept. For this purpose, a ferrofluid composed by magnetic nanoparticles and a ternary NADES was chosen as extractant solvent, and gas chromatography coupled to mass spectrometry was used as measurement technique.

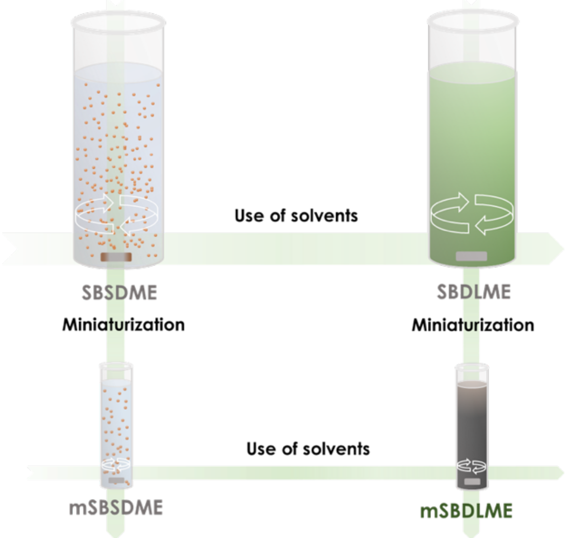

Figure 1. Scheme of the stir bar dispersive-like microextraction techniques

Acknowledgements

This contribution is based upon work from the National Thematic Network on Sample Treatment (RED2022-134079-T) of the Spanish Ministry of Science and Innovation, and the Sample Preparation Study Group and Network supported by the Division of Analytical Chemistry of the European Chemical Society. J.G. thanks the Spanish Ministry of Universities and the Next Generation-EU for his postdoctoral grant.

References

[1] C. Azorín, J.L. Benede, A. Chisvert, New challenges in sample preparation: Miniaturized stir bar sorptive dispersive microextraction as a high-throughput and feasible approach for low-availability sample preparation, Anal. Chim. Acta 1238 (2023) 340627.

[2] A. Chisvert, J.L. Benedé, J.L. Anderson, S.A Pierson, A. Salvador, Introducing a new and rapid microextraction approach based on magnetic ionic liquids: Stir bar dispersive liquid microextraction, Anal. Chim. Acta 983 (2017) 130–40.

Synthesis and Characterization of a Molecularly Imprinted Polymer for Selective Extraction of Chlordecone from Water and Biological Samples

O-36

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Keywords: *Bovine serum, Chlordecone, LC-MS/MS, Molecularly imprinted polymers, Solid-phase extraction*

The organochlorine pesticide chlordecone (CLD) was used on a massive scale until the 1990s to protect banana crops from the banana weevil in the French West Indies [1]. Even after more than 30 years, environmental compartments are still heavily contaminated (water and 15% of agricultural land in Guadeloupe or 19% in Martinique is more or less heavily polluted) [2]. This leads to indirect contamination of locally raised animals (chickens, pigs, etc.) and thus to an indirect exposure of local residents. According to “Santé Publique France”, over 90% of adults living in this area have traces of CLD in their blood. This pesticide is an endocrine disruptor and has negative effects on the cognitive and motor development of infants. In order to have a better idea of the overall exposure of local populations to CLD via the diet, it is therefore important to develop an extraction method for this pesticide from the various types of samples targeted.
Today, carcasses are submitted to official controls based on perirenal fat CLD determination, and there is no method for directly measuring CLD in water. In the first step of the study and in order to allow pre-slaughter controls, a selective analytical method based on molecularly imprinted polymer (MIP) was developed to determine the level of CLD in cattle serum that can be collected before slaughter [3-4]. Different synthesis conditions were therefore assayed by varying the nature of the monomer and of the porogen and the most promising MIP in terms of selective retention for CLD (extraction recovery of 96% % on MIP and 6 % on the non-imprinted polymer, NIP) was completely characterized by solid phase extraction (repeatability of the extraction procedure, of the synthesis and of the cartridge filling) in pure medium (Figure 1A). The capacity of the MIP was then determined at 0.13 µmole of CLD per g of MIP. The selective retention was maintained when applying the MIP to a spiked bovine serum sample (87% and 21% on the MIP and the NIP respectively) [3-4]. Moreover, on the use of the MIP led to a cleaner extract as compared to the one issued from a conventional C18 sorbent (Figure 1B), and ultimately to a limit of quantification divided by 3 (4.4 ng.L^{-1} for the whole analytical procedure in serum).

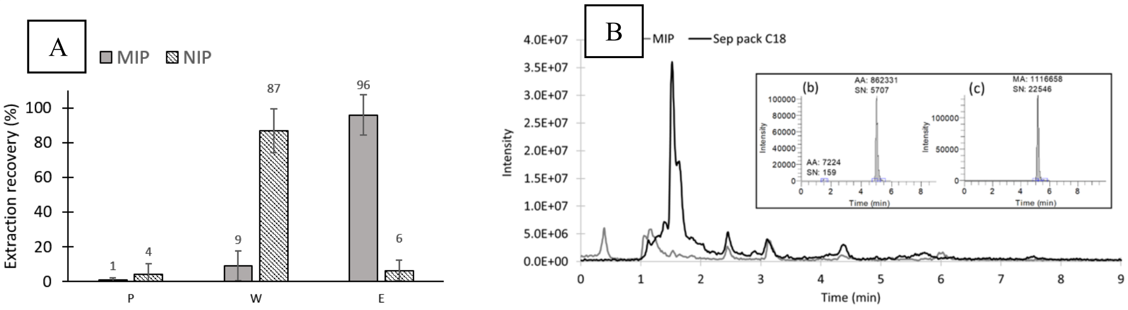

Figure 1. A- Extraction profiles obtained after percolating in triplicate 1 mL ACN spiked at 200 µg L^{-1} with CLD on three cartridges containing MIP/NIP particles issued from three independent synthesis (n=9, percolation (P), ; washing (W), elution (E). **B-** Base peak LC-MS-chromatograms (scan mode, m/z 100 -1000) corresponding to the elution fraction obtained after the percolation of 0.5 mL of serum’s extract spiked at 10 µg L^{-1} with CLD on MIP (gray line) and on Sep pack C18 (black line). The insert corresponds to the MRM chromatograms for CLD (506.7 → 426.7) corresponding to the elution fraction issued of Sep pack C18 sorbent (b) or MIP (c) [4].

Once the applicability of the extraction procedure for bovine serum had been demonstrated, a second part of the study focused on optimizing the extraction procedure so that it could be applied to extract CLD from water samples to improve method sensitivity. Particular attention was paid to increasing the enrichment factor to enable quantification of CLD in water where its concentration is extremely low, while maintaining selective retention on the MIP as compared to NIP.

References

[1] Le Déaut J-Y, Procaccia C. Impacts de l’utilisation de la chlordécone et des pesticides aux Antilles : bilan et perspectives d’évolution - Sénat. (https://www.senat.fr/notice-rapport/2008/r08-487-notice.html).
[2] A. Fournier, C. Feidt, M-L. Lastel, H. Archimede, J.P. Thome, M. Mahieu, G. Rychen, Chemosphere 2017, 171, 564–570.
[3] P. Bosman, A. Combès, M. Lambert, G. Lavison Bompard, V. Pichon, Polymère à empreintes moléculaires, et son utilisation dans la quantification d’un pesticide dans un échantillon. Patent FR2108363. 30/07/2021.
[4] P. Bosman, A. Combès, M. Lambert, G. Lavison-Bompard, V. Pichon, Development and Application of Molecularly Imprinted Polymers for the Selective Extraction of Chlordecone from Bovine Serum, Separations (2021) 8 (12) 237.

Smart Sampling: "Spot-on" for Advanced Protein Determination from Dried Matrix Spots

O-37

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Keywords: *Dried blood spots, Integrated sample preparation, Lab-on-paper, LC-MS/MS, Protein determination*

Determination of biological active compounds from dried matrix spots is a widely accepted standard in newborn screening and becomes increasingly popular for other purposes. Collection of samples (in most cases whole blood) in this sustainable manner allows for sampling of tiny amounts (few microliters) from patients or test animals. In addition, sampling can be performed at home without the need of trained personnel and the samples can be transported without the necessity of refrigeration.

Many compound classes can be measured from dried matrix spots, but the focus in this presentation will be on the determination of proteins from dried matrix spots using liquid chromatography mass spectrometry (LC-MS). This field still is in its infancy. Not only are these analyses advanced, also a lot of time and effort needs to be put into the sample pretreatment to get satisfactory results. Two pretreatment steps are essential in analysis of proteins from biological matrices by LC-MS: selective affinity capture using monoclonal antibodies and enzymatic digestion for bottom-up analysis.

The research in our group focusses on integrating these steps in the initial stage of the sampling workflow. It saves both time and simplifies the work to be carried out in the laboratory. This concept is called "smart sampling".

Smart samplers are designed such that the sample pretreatment already starts at the moment of sampling and proceeds during drying of the matrix. When the smart sampler arrives at the laboratory, only short time and little effort is needed before the analysis can be carried out. The smart samplers are prepared through covalent binding of monoclonal antibodies (to integrate affinity capture) or trypsin (to integrate proteolysis) to regular filter paper. Besides biopolymers like cellulose, also other materials used in blood collection (VAMS) can serve as starting point for production of smart samplers.

This presentation gives an overview of our efforts made to develop the concept of smart samplers for affinity capture or tryptic digestion of proteins. Several approaches of affinity capture smart samplers (see figure 1) will be highlighted. The potential of smart sampling in advanced protein analysis will be discussed through its validated performance.

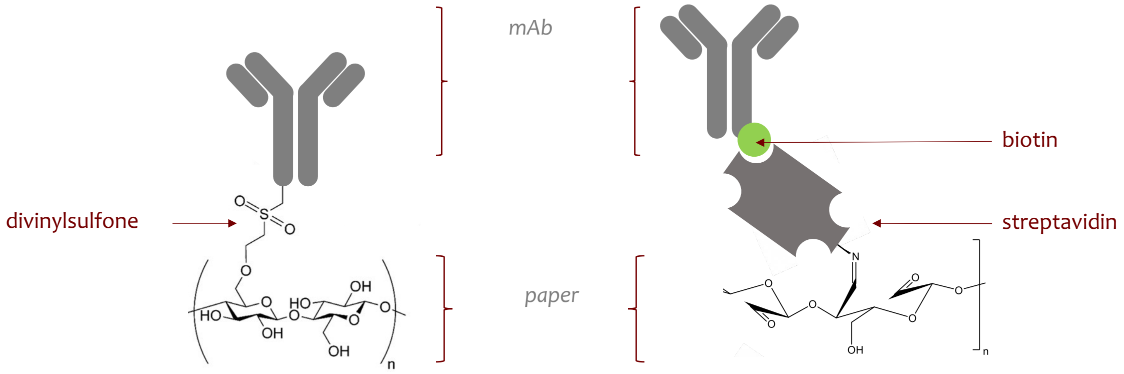

Figure 1. Two examples of attaching mAb´s to cellulose. This gives smart samplers which can capture target proteins from a single droplet of biological matrix dripped on the filter-paper.

References

[1] Øystein Skjærvø, Eirik J. Solbakk, Trine Grønhaug Halvorsen, Léon Reubsaet. Paper-based immunocapture for targeted protein analysis. Talanta 195 (2019) 764-770.

[2] Minh Thao Nguyen, Trine Grønhaug Halvorsen, Bernd Thiede, Léon Reubsaet. Smart proteolysis samplers for pre-lab bottom-up protein analysis – Performance of on-paper digestion compared to conventional digestion. Separation Science Plus 5 (2022) 171-183

[3] Léon Reubsaet, Bernd Thiede, Trine Grønhaug Halvorsen. Next generation VAMS®–Trypsin immobilization for instant proteolysis in bottom-up protein determination. Advances in Sample Preparation 3 (2022) 100027

[4] Christina Johannsen, Léon Reubsaet, Trine Grønhaug Halvorsen. On the spot immunocapture in targeted biomarker analysis using paper-bound streptavidin as anchor for biotinylated antibodies. Analytical and Bioanalytical Chemistry 414 (2022) 5979-5989

[5] Ago Mrsa, Greta Nardini, Trine Grønhaug Halvorsen, Bernd Thiede, Léon Reubsaet. One-step functionalization of paper and simplified antibody immobilization for on-the-spot immunocapture from dried serum in liquid chromatography-tandem mass spectrometry based targeted protein determination. Journal of Mass Spectrometry (2024).

New Amphoteric Materials for Sorptive Extraction

O-38

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Keywords: *Amphoteric materials, Contaminants, Environmental water samples, Iion-exchange interactions, Solid-phase extraction*

Amphoteric materials that combine cation-exchange and anion-exchange interactions have been already synthesised using silica- or polymer-based skeleton (reversed-phase interactions) functionalised with the amphoteric moieties [1,2]. Nevertheless, when these materials are applied in extraction protocols, the selective retention of both acidic and basic analytes together was difficult to achieve which was attributed to charge repulsion between charges. In previous studies [2,3] hypercrosslinked polymers were functionalised with amino acid amphoteric moieties (namely quaternised sarcosine and taurine) which involve a distance of two carbons between the acidic and the basic moieties.

Considering that the closeness of the ionic groups may involve repulsion problems, in the present study, a new amphoteric material was prepared using an alternative two-step approach that includes the functionalization of the hypercrosslinked particles with maleic anhydride that was further ring-opening using ethylenediamine (Figure 1 shows the complete synthetic route), with a distance between both ionic moieties (carboxylic acid and primary amine) of seven carbons that may prevent from charge repulsion between them.

The new material presents weak cation exchange (WCX) and weak anion exchange (WAX) interactions simultaneously and it was evaluated in the solid-phase extraction (SPE) followed by liquid chromatography with high resolution mass spectrometry (LC-HRMS) for the selective determination of a group of acidic and basic pharmaceuticals from complex environmental waters. The SPE parameters such as sample pH, washing and elution conditions were carefully optimised to exploit these ionic interactions between compounds and the functional groups. When loading 100 mL of ultrapure water followed by the optimised SPE protocol, the new amphoteic sorbent provided recoveries higher than 80% for all the compounds.

The new amphoteric material was further validated and applied to the extraction of 100 mL of river, 50 mL effluent and 25 mL of influent sewage water samples with apparent recoveries ranging from 34% and 112% for all the compounds, with the exception of metroprolol and trimetoprim, and matrix effect lower than ±20% in most cases thanks to the inclusion of an effective washing step based on methanol.

Moreover, this method was applied to determine the presence of the selected compounds in these samples and the selected analytes were successfully quantified in the samples at ng L^{-1} levels.

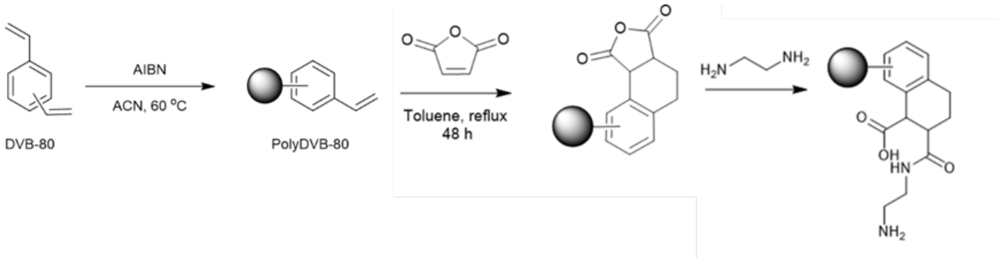

Figure 1. Scheme of the synthesis of the developed material.

Acknowledgements

These results are part of the project PID2020-114587GB-I00 funded by MCIN/AEI/10.13039/501100011033. A. Moral would also like to thank Universitat Rovira i Virgili (URV) for his PhD grant (2020PMF-PIPF-33).

References

[1] A. Moral, P. Clivillé-Cabré, F. Borrull, K.G. Furton, A. Kabir, R.M. Marcé, N. Fontanals, Adv. Sample Prep. 7 (2023) 100074.
[2] J.C. Nadal, S. Dargo, F. Borrull, P.A.G. Cormack, N. Fontanals, R.M. Marcé, J. Chromatogr. A. 1661 (2022) 462715.
[3] J.C. Nadal, K.L. Anderson, S. Dargo, I. Joas, D. Salas, F. Borrull, P.A.G. Cormack, R.M. Marcé, N. Fontanals, J. Chromatogr. A. 1626 (2020) 461348.

Preconcentration of Bioactive Compounds by New Sorbent Materials: Searching for Sustainability in Solid-Phase Extraction

O-39

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Keywords: *Biochar, Pharmaceuticals, Porous polymers, Sample preparation, Trace analysis*

The development of sustainable sorbents is a hot research topic in analytical chemistry to improve the greenness of sample preparation. New extraction phases should combine extraction efficiency and reusability, and the environmental impact in their application should be minimized [1,2]. In this context, polymers are attractive owing to their low cost, robustness, and reusability, and nature-derived materials are catching great interest due to their large availability from renewable sources, and low toxicity [1]. For example, biochar shows good sorption behavior towards a wide range of compounds, making it a valid candidate for implementing solid-phase extraction (SPE) protocols [3]. This communication presents the sustainability evaluation of porous polymers and biochar as two different types of alternative SPE sorbents for bioactive compounds, i.e. steroid hormones and fluoroquinolones as water contaminants. Porous polymers from high internal phase emulsions are synthesized via drop-by-drop addition of an aqueous solution to an organic phase, under stirring. The resulting material shows a peculiar inner structure made of voids each other interconnected by holes, well suited for analytical in-flow processes and sample treatment [4,5]. In this work, reversed-phase porous polymers were one-pot prepared at room temperature and tested for multiclass extraction of steroids. The polymer affinity for the targets was tuned by varying the composition to simultaneously retain glucocorticoids, progestins, androgens and estrogens (logP 1.46-4.01). SPE trials (10 mL tap water, spike 1 mg L^{-1}, 200 mg packed-cartridge) were performed on four different polymer compositions, evidencing a quantitative uptake of sex hormones from the solution (92-100%, RSD < 15%, *n=3*), but lower efficiency towards glucocorticoids. These are the most hydrophilic compounds among the considered steroids, and accordingly it was found that the addition of PEG methacrylate (Mn 360) in the pre-polymerization mixture to get a proper hydrophilic-lipophilic balance enhances their sorption up to 85%. After uptake, all the analytes are fully eluted by a single fraction of ethanol (2 mL), with recovery around 90% for sex hormones and in the range 40-80% for glucocorticoids (RSD < 17%, *n=3*). Based on these results and considering the cartridge reusability for at least four samples, further work is underway at lower concentrations. Another sort of reverse phase, biochar, has been prepared by pyrolysis (650°C, 6 h) of wastes from the agri-food sector, i.e. pumpkin, melon, and orange peels, and used in packed cartridges (50 mg) in tap water samples (50 mL, native pH) enriched with sex hormones or fluoroquinolones (50 µg L^{-1}). Adsorption was quantitative on all the prepared biochar, with a successive elution by 1 mL of 10 mM TBAH aqueous solution (15% v/v acetonitrile) for the antimicrobials and 2 mL ethanol for steroids. To simplify the extraction procedure avoiding the packed-cartridge format and, accordingly, vacuum or peristaltic pumps, and to increase the sample throughput, biochar was immobilized all over the inner wall of Falcon™ tubes, with good reproducibility. In this way, the extraction was carried out simply filling the tube with the sample, placed on a rotating plate (300 rpm, 20 samples processed at once). The preliminary sorption tests in tap water (40 mL), with no pH modification, provided promising results, with steroids' uptake from 50 to 70% (RSD < 15%, *n=3*) in 1 h equilibration, maintained for several consecutive extractions, followed by elution with 3 mL ethanol (5 min shaking). Additional work is ongoing to optimize this extraction system to be later tested in environmental water samples.

Acknowledgements

This research is in the framework of the "PON Ricerca e Innovazione" Ph.D project of Petra Bianchini, DOT1322889-10, D.M. 10-08-2021, n° 1061, supported by "Ministero dell'Università e della Ricerca (MUR)" and the European Union, and of the NODES project supported by MUR – M4C2 1.5 of PNRR funded by the European Union - NextGenerationEU (Grant agreement no. ECS00000036). The authors acknowledge the support of MUR and the University of Pavia through the program "Dipartimenti di Eccellenza 2023-2027", and of Regione Lombardia (Italy), Project CE4WE (Circular Economy for Water and Energy), ID 1139857, Call "Hub Ricerca e Innovazione".

References

[1] X. Ma, L. Wang, Q. He, Q. Sun, D. Yin, Y. Zhang, A review on recent developments and applications of green sorbents-based solid phase extraction techniques, Adv. Sample Prep. 6 (2023) 100065.
[2] F. Merlo, A. Profumo, A. Speltini, Sample treatment for the determination of steroid hormone contaminants in water samples: analytical greenness assessment, Trends Anal. Chem. 169 (2023) 117393.
[3] H. Zhang, S. Zhang, Y. Li, L. Li, X. Hou, Biochar/sodium alginate mixed matrix membrane as adsorbent for in-syringe solid-phase extraction towards trace nitroimidazoles in water samples prior to ultra-high-performance liquid chromatography-tandem mass spectrometry analysis, J. Sep. Sci. 46 (2023) 2300316.
[4] J. Luo, Z. Huang, L. Liu, H. Wang, G. Ruan, C. Zhao, F. Dou, Recent advances in separation applications of polymerized high internal phase emulsions, J. Sep. Sci. 44 (2021) 169-187.
[5] F. Merlo, F. Colucci, G. De Soricellis, F. Rinaldi, E. Calleri, A. Profumo, A. Speltini, Carbon nanotubes in high internal phase emulsion polymer composite for packed-cartridge micro-solid-phase extraction of fluoroquinolones in urine, Adv. Sample Prep.

9 (2024) 100103.

Planar Sorptive Phases, from Thin Films to Polymeric Coated Particles

O-40

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Keywords: *Mass spectrometry, Planar sorptive phases, Polymeric particles, Thin film*

The use of planar sorptive phases in microextraction has gained interest thanks to their higher extraction capacity derived from the larger surface available for interaction with the target analytes. Moreover, they can be easily prepared in different formats and sizes. If a flexible substrate is selected, these phases can also be adapted to different microextraction formats (e.g., in-vial, pipette-tip) and sample volumes (Figure 1a). In addition, the material used to create the thin film can cover a wide variety of polarities and interaction chemistries [1], thus permitting it to be tailored according to the analytical problem to be solved. If a natural support (e.g., cellulose) is selected, the resulting sample preparation contributes to the sustainability of the whole analytical process [2].

In spite of these advantages, the extraction capacity of planar sorbent phases is somehow jeopardized due to the low final porosity they present. A simple way to improve this extraction capacity while preserving the advantages of sorbent phases is the substitution of the continuous polymeric coating with a particulate thin film. As can be seen in Figure 1b, a high homogeneous distribution of the particles can be obtained once they contact an adherent support. The presence of the particle over the planar surface permits free interaction with the analytes.

This distribution not only increases the surface area, but additional interaction chemistries depending on the nature of the particles. They can vary from balanced hydrophilic-lipophilic interactions (e.g., HLB particles) [3] to ionic exchange (e.g., MCX particles) [4]. The resulting phase is efficient, the preparation procedure is simple and affordable, and they can be easily coupled to a high-resolution mass spectrometer, which also increases the sample throughput.

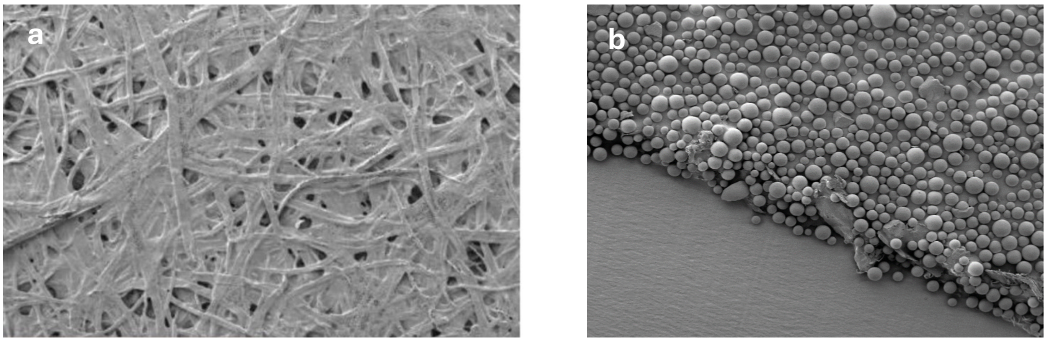

Figure 1. Images of a) cellulose support coated by a polymeric film and b) coated with particles. Reproduced form references [1] and [4] under creative commons license.

Acknowledgements
Financial support from the Spanish Ministry of Science and Innovation (grant PID2020-112868RB) is gratefully acknowledged.

References

[1] J.L. Benedé, A. Chisvert, R. Lucena, S. Cárdenas, A paper-based polystyrene/nylon Janus platform for the microextraction of UV filters in water samples as proof-of-concept, Microchim. Acta 188 (2021) 391.
[2] M. González-Bermudez, A.I. López-Lorente, R. Lucena, S. Cárdenas, Paper-based sorptive phases for a sustainable sample preparation, Advances in Sample Preparation 5 (2023) 100051.
[3] F.A. Casado-Carmona, J.M. Jiménez-Soto, R. Lucena, S.Cárdenas, Portable stirring device for the on-site extraction of environmental waters using magnetic hydrophilic-lipophilic balance tape, Anal. Chim. Acta 1189 (2022) 339186.
[4] C. Calero-Cañuelo, F.A. Casado-Carmona, R. Lucena, S. Cárdenas, Sorptive tape-spray tandem mass spectrometry using aluminum foil coated with mixed-mode microparticles, Talanta 272 (2024) 125774.

9. Young Researchers Presentations

In Vitro Bioaccessibility Assessment of Tire Related Compounds, Including 6PPD and 6PPDq, Using Simulated Fluids

YO-1

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Keywords: *In vitro bioaccessibility, LC-MS/MS, Recycled tire crumb rubber (RTCR), Solid phase extraction (SPE)*

Once the tire life ends with respect to its initial use on the roads, the most conventional way to give a second life to this residue is to shred it getting crumb rubber as final by product. This recycled tire crumb rubber (RTCR) is mainly used on daily surfaces such as playgrounds, tree retainers or infill on synthetic football fields. In September 2023, the European Commission banned the use of RTCR on synthetic fields giving manufacturers 8 years to replace the material, as RTCR represents the main source of intentionally added microplastics in the environment [1]. The composition of this material is virtually the same as that of pneumatics, containing hydrocarbon aromatic polycycles (PAHs), metals [2] and tire related compounds including antiozonants, such as 6PPD or 6PPDq [3], both linked to the death of aquatic species [4].

The aim of this work is to evaluate the oral bioaccessibility of tire related compounds, including antiozonants and vulcanizants agents coming from real samples of RTCR using simulated biological fluids. For this purpose, the Unified Bioaccessibility Method (UBM) [5] was selected to simulate the ingestion of the material. Real RTCR samples were brought into contact with four biological fluids (saliva, gastric and duodenal juice, and bile) in an attempt to simulate human digestion.

Then, the organic compounds present in the mixture were extracted by Solid Phase Extraction (SPE). This extraction process has been optimized to obtain the best extraction conditions. Besides, ultrasound assisted extraction was performed to evaluate the total concentration of the target compounds in the matrix. Liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) was the selected technique to identify and quantify the target compounds.

The results showed the *in vitro* bioaccessibility of all analytes studied. This bioaccessibility ranged from 0.01% to a high percentage, depending on the compounds. Benzothiazole (BTZ) showed the highest oral bioaccessibility.

Acknowledgements

The authors thank projects PID2022-140148OB-I00, RED2022-134079-T and RETOSPID2019-104336RB-I00 (Ministry of

Science, Innovation and Universities, Spain), ED431B 2023/04 and IN607B 2022/15 (Galician Competitive Research Groups, Xunta de Galicia). This study is also based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society. All these programs are co-funded by FEDER (UE).

References

[1] Commission Regulation (EU) 2023/2055. 2023.
[2] M. Celeiro, T. Dagnac, M. Llompart. Chemosphere. 195 (2018) 201-211.
[3] A. Duque-Villaverde, D. Armada, T. Dagnac, M. Llompart. Sci. Total. Environ. 929 (2024) 172674.
[4] Tian et al. Science. 371.6525 (2021) 185-189.
[5] BARGE-INERIS. UBM procedure for the measurement of inorganic contaminant bioaccessibility from solid matrices (2010).

Vacuum-Assisted Headspace Solid-Phase Microextraction of Tomato Volatiles During Ripening

YO-2

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***Keywords**: Headspace solid phase microextraction, Ripening, Tomato, Vacuum, Volatiles*

The aroma quality of tomatoes significantly influences consumer perception and acceptability, resulting from a delicate balance of sugars, acids, and volatile organic compounds (VOCs). Despite their crucial role, modern fresh tomatoes often lack flavor, as breeding innovations have prioritized other qualitative attributes over volatile compounds [1,2]. Headspace solid phase microextraction (HS-SPME) has emerged as a valuable tool for exploring the volatile profile of tomatoes and tomato-based products, offering advantages such as simplicity, rapid analysis, and solvent-free operation [3,4]. This study aimed to investigate changes in the volatile profile of *Solanum Lycopersicum* Ailsa Craig tomatoes during ripening using vacuum-assisted HS-SPME (Vac-HS-SPME) for the first time. Optimization of extraction parameters, including time and temperature, under both vacuum and atmospheric pressure conditions, preceded the evaluation and comparison of Vac-HS-SPME and HS-SPME performance. By air-evacuating the sample container after introducing the sample, we expected to accelerate the extraction kinetics of analytes with a low affinity for the headspace [5]. The results showed that Vac-HS-SPME surpassed conventional HS-SPME in both the number of detected compounds and overall extraction efficiency, performing consistently better across various time and temperature combinations. Optimal conditions for Vac-HS-SPME were determined to be a sampling time of 45 minutes at 40 °C, contrasting with 60 °C required for HS-SPME. The study also evaluated the volatile profile across six ripening stages, highlighting aldehydes, particularly hexanal and (E)-2-hexenal, as predominant compounds throughout ripening, with concentrations peaking at the red stage. Vacuum conditions at 40 °C increased concentrations of aldehydes and alcohols compared to atmospheric pressure at 60 °C.

Acknowledgements

This work was funded by the Hellenic Foundation for Research and Innovation (HFRI).

References

[1] G. Kaur, M. Abugu, D. Tieman, The dissection of tomato flavor : biochemistry , genetics , and omics, Front. Plant Sci.14 (2023) 1–18.
[2] R.P. Mauro, D. Page, F. Giuffrida, N. Bertin, C. Leonardi, Aroma volatiles in tomato fruits: The role of genetic, Agron. J. 12 (2022) 1-27.
[3] J. Figueira, H. Câmara, J. Pereira, J.S. Câmara, Evaluation of volatile metabolites as markers in Lycopersicon esculentum L. cultivars discrimination by multivariate analysis of headspace solid phase microextraction and mass spectrometry data, Food Chem. 145 (2014) 653–663.
[4] J. Li, Y. Fu, X. Bao, H. Li, J. Zuo, Optimization of solid phase microextraction combined with gas chromatography-mass spectrometry (GC-MS) to analyze aromatic compounds in fresh tomatoes, J. Food Biochem. 43 (2019) 1–12.
[5] E. Psillakis, The effect of vacuum: an emerging experimental parameter to consider during headspace microextraction sampling, Anal. Bioanal. Chem. 412 (2020) 5989-5997.

Advancements in LC-MS/MS Methodology: Quantification of Six Phosphatidylethanol Homologues in Whole Blood with Minimized Phospholipid Interference

YO-3

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Keywords: *Alcohol consumption, LC-MS/MS, Liquid-liquid extraction (LLE), Phosphatidylethanol, Phospholipid removal*

Alcohol consumption is undeniably linked to a multitude of health risks, injuries, and even death, and has significant social and economic consequences worldwide [1]. Phosphatidylethanol (PEth), is a group of promising direct alcohol biomarkers, with a considerably longer half-life in blood compared to ethanol. These biomarkers can be measured to predict various patterns of alcohol consumption [2]. This study's goal was to develop and validate an accurate and precise LC-MS/MS method for detecting six PEth homologues in whole blood, while minimizing interference from unwanted phospholipids. Different organic solvent mixtures for liquid-liquid extraction were investigated aiming to achieve optimal recovery of PEth homologues while eliminating lyso-phospholipids and other interfering phospholipids. For the instrumental analyses, was used an LC-MS/MS. For chromatographic separation was used a BEH C18 column. The mobile phase consisted of 0.025% ammonia in Type I water, pH 10.7, as solvent A, and methanol as solvent B [3]. After method optimization, it was found that the mixture of heptane/2-propanol (80:20, v:v) provided the lowest phospholipid background, satisfactory recovery of all six PEth homologues, and the best signal-to-noise values. The method validation was performed by using blank whole blood as matrix in calibrators and QC samples. Lower limit of quantification was 10 nM for all compounds. The extraction recoveries obtained were within 37-51% and no matrix effects were observed. Quantification of 22 authentic blood samples showed that the developed LC-MS/MS method is sensitive, precise and accurate for the determination of the six PEth homologues in whole blood [4].

Acknowledgements

This work was financed by national funds through Fundação para a Ciência e a Tecnologia (FCT), under the Project UIDB/04585/2020. Centro de Química Estrutural is a Research Unit funded by FCT through projects (PIDDAC - UIDB/00100/2020 and UIDP/00100/2020). Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. Marisa Henriques Maria is grateful to acknowledge her PhD grant no. 2022.10965.BDANA awarded by Fundação para a Ciência e a Tecnologia.

References

[1] WHO, J. H. Hammer, M. C. Parent, and D. A. Spiker, Global status report on alcohol and health 2018, 65(2018)
[2] A. W. Jones, "Evidence-based survey of the elimination rates of ethanol from blood with applications in forensic casework," Forensic Sci Int, vol. 200, no. 1–3, pp. 1–20, 2010
[3] M. H. Maria, B. M. Jørgenrud, and T. Berg, "Determination of eight phosphatidylethanol homologues in blood by reversed phase liquid chromatography–tandem mass spectrometry – How to avoid co-elution of phosphatidylethanols and unwanted phospholipids," J Chromatogr A, vol. 1684, p. 463566, 2022
[4] M. Maria, N. R. Neng, and T. Berg, "An accurate and precise liquid chromatography–tandem mass spectrometry method for the determination of six phosphatidylethanol homologues in whole blood with phospholipid interferences minimized," J Chromatogr A, 1711, p. 464451, 2023.

Coupling Miniaturized Stir Bar Sorptive Dispersive Microextraction to Needle-Based Electrospray Ionization Emitters for Mass Spectrometry

YO-4

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Keywords: *Bioanalysis, Coupling, Mass spectrometry, Microextraction, Needle-based emitter*

Direct combination of sample preparation strategies and mass spectrometry (MS) detection has emerged as a valuable alternative to classical analytical approaches that typically intercalate a separation technique (*i.e.*, chromatography) between them [1]. The bypass of the chromatographic separation can speed up analysis, enabling faster decision-making.

In such combinations, where the analysis time is mainly defined by the extraction procedure, magnetic dispersive solid-phase extraction emerges as a relevant technique because of its rapid workflow. The dispersion and retrieval of the magnetic sorbent are typically uncoupled stages, thus reducing the potential simplicity. Stir bar sorptive dispersive microextraction (SBSDME) is a novel technique that integrates both stages in a single device. Its recent miniaturized version (mSBSDME) makes the approach more portable and compatible with low-volume samples [2].

In this communication we describe the direct coupling of mSBSDME and MS using a needle-based electrospray ionization (NESI) emitter as the interface. As a proof-of-concept, this coupling is applied to determine tetrahydrocannabinol in saliva samples, a relevant societal problem if the global consumption rates of cannabis are considered. The coupling only requires the transference of the magnet (containing the sorbent and the isolated analyte) from the mSBSDME to the hub of a hypodermic needle, where the online elution occurs. The application of 5 kV on the needle forms an electrospray on its tip, transferring the ionized analyte to the MS inlet. The excellent performance of mSBSDME-NESI-MS/MS relies on the sensitivity (limits of detection as low as 2.25 ng mL^{-1}), the precision (relative standard deviation lower than 15%), and the accuracy (relative recoveries ranged from 87 to 127%) obtained. According to the obtained results, mSBSDME-NESI-MS/MS technique promises faster and more efficient chemical analysis in MS-based applications.

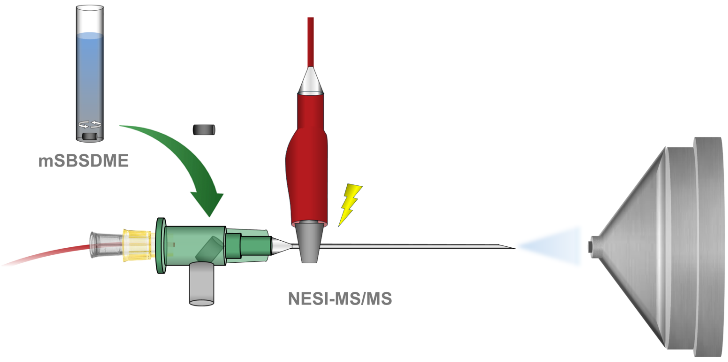

Figure 1. Schematic diagram of the proposed mSBSDME-NESI-MS/MS procedure.

Acknowledgements

Grants PID2020-118924RB-I00 and PID2020-112862RB-I00, funded by MICIU/AEI/ 10.13039/501100011033, are greatly appreciated. A.L.L.-J. also thanks the Generalitat Valenciana for the INVESTIGO contract through the project INVEST/2022/109. J.M.-S. expresses his gratitude for the predoctoral grant (FPU19/01488) from the Spanish Ministry of Universities. This article is based upon work from the National Network for Sustainable Sample Preparation (RED2022-134079-T funded by MICIU/AEI/ 10.13039/501100011033) and the Sample Preparation Study Group and Network supported by the Division of Analytical Chemistry of the European Chemical Society.

References

[1] G.A. Gómez-Ríos, M.F. Mirabelli, Solid Phase Microextraction-Mass Spectrometry: Metanoia, TrAC - Trends Anal. Chem. 112 (2019) 201–211.

[2] C. Azorín, J.L. Benedé, A. Chisvert, New Challenges in Sample Preparation: Miniaturized Stir Bar Sorptive Dispersive Microextraction as a High-Throughput and Feasible Approach for Low-Availability Sample Preparation, Anal. Chim. Acta 1238 (2023) 340627.

Gas-Diffusion Microextraction as a Sustainable Sample Preparation to Determine Fragrance Allergens

YO-5

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Keywords: *Fragrance allergens, Cosmetics, Personal care products, Gas-diffusion microextraction, GC-MS*

Gas-Diffusion Microextraction is an extraction technique in which the analytes are separated from the sample by a microporous gas-permeable membrane (diffusion) into a small volume of extraction/acceptor solution. This technique is based on the diffusion of the analytes, so it is applied for volatile and semi-volatile compounds [1,2].

An efficient and cost-effective sample preparation gas-diffusion microextraction (GDME) methodology followed by gas chromatography coupled to tandem mass spectrometry (GC-MS/MS) is proposed for the first time to determine fragrance allergens in water-based and alcohol-based cosmetic products. The experimental conditions have been optimized by an experimental design evaluating the influence of six parameters: volume of acceptor solvent, percentage of acetonitrile in the acceptor solvent, sample dilution, salting-out effect, extraction time and volume of sample. Under the optimized conditions, the method was validated in terms of linearity, precision, accuracy, and greenness. The absence of significant matrix effects allowed quantification in real samples by external calibration. The wide used of these cosmetic ingredients in real samples is demonstrated.

Acknowledgements

This research was supported by projects UNST10-1E-491 (Infrastructure Program, Ministry of Science and Innovation, Spain), ED431B 2023/04 and IN607B 2022/15 (Consolidated Research Groups Program, Xunta de Galicia). The authors belong to the National Network for Sustainable Sample Preparation, RED2022-134079-T (Ministry of Science, Innovation and Universities, Spain). This study is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society. M.L. acknowledge the IUPAC project 2021-015-2-500: Greenness of official standard sample preparation methods. A.C.L. acknowledges the Xunta de Galicia predoctoral contract (ED481A and IN606A).

References

[1] J. G. Pacheco, I. M. Valente, L. M. Gonçalves, J. A. Rodrigues, A. A. Barros, Gas-diffusion microextraction. J. Sep. Sci. 33 (2010) 20, 3207-3212.

[2] A. Custodio-Mendoza, J. Aja-Macaya, I. M. Valente, J. A. Rodrigues, P. J. Almeida, R. A. Lorenzo, A. M. Carro, Determination of malondialdehyde, acrolein and four other products of lipid peroxidation in edible oils by Gas-Diffusion Microextraction combined with Dispersive Liquid-Liquid Microextraction, J. Chromatogr. A. 1627 (2020) 461397.

Biomimetic Tools for Selective Solid-Phase Extraction of Pesticides in Water Intended for Human Consumptions

YO-6

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Keywords: *Green sample preparation, Molecularly imprinted polymers, Oligosorbents, Solid-phase extraction*

The recast of EU Drinking Water Directive (2020/2184) aims to promote a risk assessment and waste management approach while facing climate change and increase in pollution. As part of the ToDrinQ project selected by the EU in 2022, OliSens in collaboration with the LSABM (UMR CBI 8231 CNRS-ESPCI Paris PSL) aims to develop new on-site and real-time pesticide monitoring devices to track the quality of the water intended for human consumption. In order to do so, a solid-phase extraction (SPE) based on a sorbent specific to the targeted molecules will constitute the key component of the final device.

The molecules targeted are atrazine and its metabolites, which are responsible for some of the main water pollution in France and Europe [1]. The targeted levels of concentration being low and the sample complex, the extraction step needs to promote a high enrichment factor. It should also be selective to allow the hyphenation of the extraction step directly with a simple and cheap detection system, without an intermediate separation step. Two approaches based on biomimetic tools have thus been considered: molecularly imprinted polymers (MIPs) and supports functionalized by aptamers (oligosorbents).

A MIP targeting atrazine and its metabolites (desethyl-atrazine (DEA) and desisopropyl-atrazine (DIA)) was synthesized using a triazine as template. Its control support, a non-imprinted polymer (NIP), was also synthesized with the same conditions but without the template molecule. The performances of the sorbents were evaluated in SPE using a procedure adapted from a previous study [2] with ultrapure water spiked at 0,1 µg/L with atrazine and its metabolites. The percolation, washing and elution fractions were analyzed by liquid chromatography coupled with ultraviolet detection (LC-UV). As expected, a high selectivity was observed with the imprinted sorbent, allowing the retention of the targeted compounds until elution on the MIP (recoveries between 77 and 84% and standard deviations (SDs) between 3 and 16%, n=3) whereas they are lost in the washing fractions on the NIP (extraction recoveries between 0 and 20% and SDs between 0 and 9%, n=3). A high enrichment factor of 400 was achieved by increasing the percolation volume and decreasing the resuspension volume before detection. However, the SPE protocol involved dichloromethane during one of the washing step and methanol for elution. To improve the greenness of the SPE protocol, methanol was successfully substituted with ethanol. Different green solvents or mixtures of green solvents were evaluated to replace the dichloromethane while maintaining selectivity and high extraction recoveries on the MIP. Dimethyl carbonate seems to be the best candidate.

Another approach was based on the synthesis of supports functionalized by aptamers reported as specific to atrazine (oligosorbents). One advantage of the use of oligosorbents rather than MIPs is that the sorbent synthesis and the SPE implements only aqueous solutions, i. e. “green solvents”. Moreover, a higher specificity can also be expected. Five different DNA sequences were identified in literature even if there is a lack of information regarding their specificity and selectivity. These sequences were grafted on CNBr-activated Sepharose such as 3 scrambled sequences to get also control supports. The resulting grafting yields were determined and are close to the usually expected values between 30 and 60%. The SPE profiles obtained with the oligosorbents were compared to the ones obtained with the MIP. The performances of potential combinations of both kinds of sorbents will be discussed.

References

[1] Direction générale de la Santé (DGS), Bilan de la qualité de l’eau du robinet du consommateur vis-à-vis des pesticides en France en 2020, Décembre 2021, https://solidarites-sante.gouv.fr/IMG/pdf/2020_bilan_pesticides_vf.pdf

[2] F. Chapuis, V. Pichon, F. Lanza, S. Sellergren, M.-C. Hennion, Optimization of the Class-Selective Extraction of Triazines from Aqueous Samples Using a Molecularly Imprinted Polymer by a Comprehensive Approach of the Retention Mechanism, J. Chromatogr. A. 999(1–2) (2003) 23–33.

Advancement of Resistive Pulse Sensing for Particle Identification and Use on Environmental Samples

YO-7

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Keywords: *Microplastics, Resistive pulse sensing*

Here we present improved techniques for identification, quantification, and characterization of Nanoplastics using Resistive Pulse Sensing [1] (RPS), a method that is capable of measuring particle size and concentration on a nano scale and applying it to environmental samples.

"WHO calls for more research into microplastics and a crackdown on plastic pollution".[2] Whist there are efforts being made to understand scale, there is a disproportionate volume of research focused on the macro and micro scale, and not enough on nano plastics, despite their increased threat to health.[3] Additionally, most research to date uses the current principal technique, Dynamic Light Scattering [4] (DLS), which is limited as the technique only provides information on particles size and is not suitable for non-monodispersed samples, due to its low resolution.

We observed that polystyrene particles are consistently attracted to charged surfaces, therefore we successfully integrated a charged surface within a preexisting flow RPS set up, microfluidic cell, using conductive tipped electrode stubs, as displayed in fig.1. The conductive electrode studs were connected to a battery whilst the environmental samples were pushed through the cell, flowing across the charged tips. The particle removal was then observed in post flow; with tunable RPS. The conductive tipped electrodes have been integrated, and optimized for salinity, flow pressure, conductive material, and applied voltage. From the data obtained it was decided that for optimal results the operating conditions should be as follows: A copper conductive material, with a pressure of 50 mbar, salinity concentration of 100 mM (KCl) and an applied voltage of 3 V.

Once optimized, environmental samples were collected from a lake, canal, and river in Leicestershire, UK (fig. 2,3) These samples were then either treated (with commonly used digestive solvents), pushed through the charged cell, or both; and collected quarterly: September 2023, December 2023, March 2024, and June 2024; to investigate fluctuations in particle concentrations over a year and the impact of varying temperature, rainfall, water levels and sunlight.

Thus far the data suggests that after heavy rain fall and flooding there is a significant increase in particles within a sample. Additionally, the use of a battery and microfluidic system decreases the particle count of the sample, as does hydrogen peroxide.

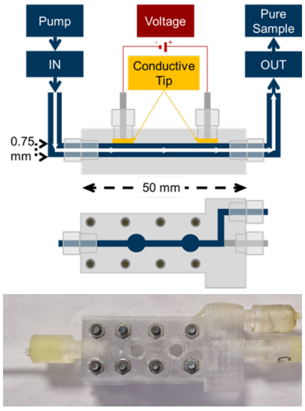

Figure 1. Diagram of repurposed microfludic cell

Figure 2. Map of UK (red spot denoting location of sampling)

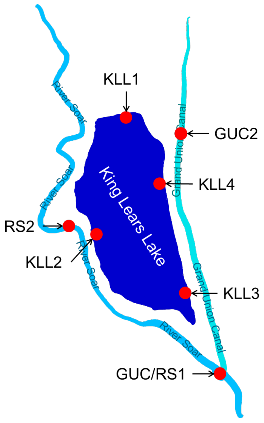

Figure 3. Map of sample site (red spot denoting location of sampling)

Acknowledgements

With thanks to Loughborough University for their studentship funding

References

[1] M. Pollard, E. Hunsicker and M. Platt, A Tunable Three-Dimensional Printed Microfluidic Resistive Pulse Sensor for the Characterization of Algae and Microplastics, ACS Sens 5 (2020) 2578–2586.

[2] Who calls for more research into microplastics and a crackdown on plastic pollution (no date) World Health Organization. Available at: https://www.who.int/news/item/22-08-2019-who-calls-for-more-research-into-microplastics-and-a-crackdown-on-plastic-pollution (Accessed: 17 April 2024).

[3] V. Kopatz, *et al.,* Micro- and nanoplastics breach the blood–brain barrier (BBB): Biomolecular Corona's role revealed, *Nanomaterials*, 13(8) (2023) 1404.

[4] A. Sehgal and T. A. P. Seery, Anomalous Dynamic Light Scattering from Solutions of Light Absorbing Polymers, Macromolecules 32 (1999) 7807–7814.

Spot Test Method for Tetracycline Using Molecularly Imprinted Polymer-Coated Paper Integrated into a Portable 3D-Printed Platform with Smartphone-Based Fluorescent Detection

YO-8

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Keywords: *BAGI metric, Molecularly imprinted polymer, On site analysis, Paper-based spot test, Smartphone-based fluorescent detection.*

The development of optical sensor-based spot testing methods enables on site detection of emerging contaminants in water samples, including pharmaceutical products. This analytical tool has gained significant interest in recent years due to its simplicity, portability, and user-friendly application, especially in areas where contamination is suspected. Tetracycline (TC) is a broad spectrum antibiotic widely used in human and animal medicine to treat microbial infections as well as aquaculture growth promoters. However, this compound is poorly absorbed by the human body and the treated animals, causing a significant release into the environment through urine and feces [1]. In this work, a molecularly imprinted polymer (MIP)-coated paper has been integrated into 3D printed platform with smartphone-based fluorescent detection for the determination of TC in water samples (Fig. 1). The MIP synthesis was performed by precipitation polymerization, which was subsequently deposited onto a glass microfiber paper. The synthesized polymer and the MIP@paper were characterized by FTIR spectroscopy, scanning electron microscopy, and EDS spectroscopy. Afterwards, a 3D printed detection platform that houses monochromatic LED strips as radiation source and a smartphone as detector have been used for determination of TC. Digital image processing was based on the RGB colour model using image J software and the red intensity channel was used as analytical signal due to its higher sensitivity. Several factors that affect the adsorption capacity and fluorescent detection have been optimized. Under optimum conditions, detection limit of 0.04 mg L^{-1} was achieved for TC and good linearity was observed up 5 mg L^{-1} (r=0.9980). The intra-day and inter-day precision expressed as relative standard deviation (%RSD) were obtained of 4.9% and 7.2 %, respectively, showing the good precision of the proposed methodology. To assess matrix effects and accuracy of the proposed method in real samples, recovery studies were performed without and with TC spiked at different concentrations (0.1 – 0.3 mg L^{-1}) to water samples, showing good recoveries in the range of 87 – 98%. Moreover, the BAGI tool was used to evaluate the practicality of the proposed method, demonstrating its advantage in terms of functionality and applicability compared to previously published HPLC and spectrofluorimetric laboratory instrumental methods.

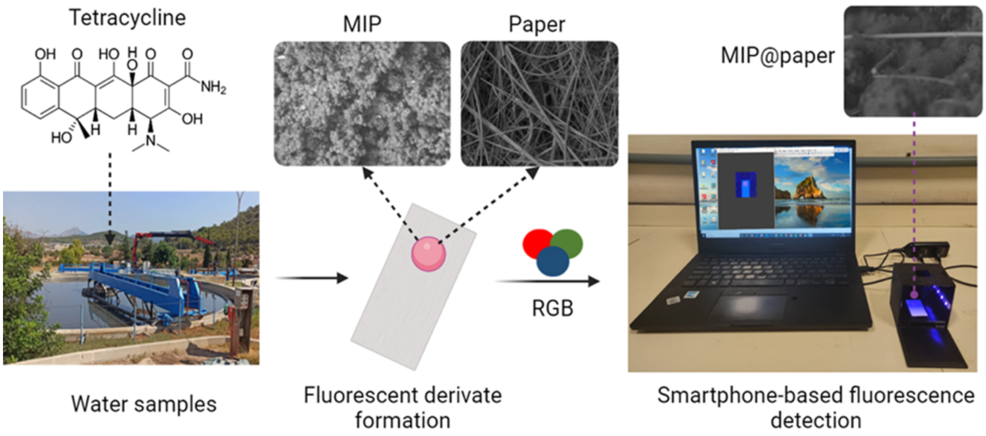

Figure 1. 3D printed portable platform with support for MIP@paper for tetracycline separation and quantification.

Acknowledgements
The authors acknowledge financial support from project PID2019-107604RB-I00 funded by MCIN/AEI/ 10.13039/501100011033 and FAPESP (Proc. 2022/03553-0). Diego Barzallo acknowledges the support from the Spanish Ministry of Science and Innovation for the pre-doctoral research fellowship (FPU20/06399).

References

[1] D.M. Ngoc, N.C. Hieu, N.H. Trung, H.H. Chien, N.Q. Thi, N.D. Hai, H.P. Chao, Tetracycline Removal from Water by Adsorption on Hydrochar and Hydrochar-Derived Activated Carbon: Performance, Mechanism, and Cost Calculation, Sustainability. 15 (2023) 4412.

High-Throughput Spectrofluorimetric Determination of Acetone in Water Samples

YO-9

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Keywords: *Acetone, Benzaldehyde derivative, Spectrofluorimetry, Solid-phase extraction, Water analysis.*

Determination of acetone in aqueous samples can be relevant for various applications, such as drinking water monitoring, wastewater reuse or biomarker studies in body fluids. In the case of water treatment, acetone such as other low-molecular-weight organic compounds can pass through ultrafiltration or reverse osmosis membranes, which are used to remove chemicals. After exposure to acetone in the aqueous phase, acetone is rapidly absorbed by the body through ingestion and dermal route, and the absorbed acetone is almost eliminated within a few days. But a study on rats drinking water containing acetone for 18 weeks revealed weight loss associated with reduced food consumption and mild kidney toxicity. Although the study was conducted on high concentrations of acetone, a long-term health effect cannot be totally excluded and has not yet been documented. It is therefore important to develop simple, rapid, and low-cost methods for the determination of acetone in aqueous samples. Methods based on spectroscopic measurements after derivatization reactions are ideal for this purpose.

At present, selective methods which do not require chromatographic separation are based on the derivatization reaction of acetone with benzaldehyde derivatives (vanillin, etc.). Unfortunately, these methods have so far had only limited applications, due to their insufficient sensitivity (ppm range) and the use of very basic solutions. The proposed method is based on the reaction with dimethylamino benzaldehyde in DMSO under moderately basic conditions, yielding a highly fluorescent compound with fluorescent wavelengths free from interferences from most other inorganic and organic compounds. Acetone contained in aqueous samples can be easily extracted and preconcentrated by solid-phase extraction with a commercial sorbent and then eluted with DMSO. The detection limits obtained are in the lower ppb range and are therefore relevant for analysis of real samples. The method was applied to real natural and wastewater samples with good agreement with reference methods.

This method has been developed in accordance with some green chemistry principles, as it requires low volumes of reagents and uses a solvent that is harmless to humans and the environment. Compared to other direct spectrometric methods, the developed method avoids the use of highly basic and corrosive solutions, and all reactions can be performed at room temperature. An on-field analytical kit for acetone could thus be easily adapted from this method using cheap blue LED as excitation source for fluorescence.

Acknowledgements

This work was funded by the French Defense Innovation Agency (AID #2021451) and Aix-Marseille University.

References

[1] Kodamatani, H.; Yoshimine, D.; Fujioka, T.; Kanzaki, R.; Tomiyasu, T. A Novel Luminol Chemiluminescence Induced by Photoexcited Ketones: A Selective Determination Method for Acetone in Wastewater. Talanta Open 3 (2021) 100035.

[2] Kozaeva, E.; Mol, V.; Nikel, P. I.; Nielsen, A. T. High-throughput Colorimetric Assays Optimized for Detection of Ketones and Aldehydes Produced by Microbial Cell Factories. Microbial Biotechnology 15(9) (2022) 2426–2438.

Cellulose Acetate Microbeads Recovered from Cigarette Filters in Packed Bed Column for Water Remediation Applications

YO-10

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Keywords: *Cellulose acetate, Cigarette butts, Recycling, Sustainable sorbent, Water treatment*

The escalating presence of diverse pollutants in our surroundings requires the development of new approaches to mitigate and reduce their detrimental effects on natural ecosystems. With the world's population growing, pressure on water resources is increasing, underscoring the urgent need for new technologies to preserve and purify them. Furthermore, the possibility of reintegrating waste materials within production cycles is functional for reducing the impact of waste on the ecosystem and the environment.

Whit this in mind, this investigation primarily focused on the recovery of cellulose acetate (CA) sourced from discarded cigarette butts (CB). A refined washing technique was applied to regenerate the raw material and its effectiveness was evaluated from the comparison of recovered and pristine polymer.

The regenerated polymer was employed in the emulsion precipitation method for the synthesis of porous microbeads. The saturated CA solution in tetrahydrofuran and sodium chloride-saturated water solution was first created. The solutions were then mixed in a ratio of 1 to 1 and magnetically stirred to promote the formation of a cloudy solution. The mQ water was gradually added to the solution to disrupt the emulsion, facilitating the precipitation of CA into microspheres (50-500 µm). Fine-tuning of the synthetic process involved systematically adjusting various procedural parameters.

To create a sorbent material capable of capturing xenobiotics from water, CA microspheres were evaluated both independently and in conjunction with activated carbon. The filler was introduced into the organic CA-THF solution and homogeneously dispersed via magnetic agitation.

The removal efficacy was assessed using a flow-through setup, packing the synthesized microbeads into glass cartridges. Optimization of sorbent quantity, active carbon dosage, and contaminated water flow rate was achieved through breakthrough curve analysis, facilitated by experimental design. Once the optimal synthesis and treatment conditions were determined, a comprehensive characterization study was conducted using SEM analysis and FTIR spectroscopy to confirm the material's composition qualitatively.

Extensive performance evaluations across more than 60 contaminants demonstrated the broad applicability and versatility of the material against various classes of xenobiotics. Competitive removal analysis elucidated the differential removal of xenobiotics with varying polarity, with retention capacities ranging from 0.5 to several dozen µg per mg.

Vacuum-Assisted SPME-GC×GC-MS for Accurate 5-HMF Determination and Volatile Profiling of Honey

YO-11

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Keywords: *5-HMF, Honey, GC×GC-MS, Multi-cumulative trapping, Vacuum-assisted SPME*

In an ever-changing world, analytical methods must evolve to adapt to increasingly precise and complex demands of the regulation, industries, and consumers. Hence, analytical methods have moved from (mono-)targeted analysis to fingerprinting and multicomponent analysis, from laborious manual extraction to fully automated sample preparation platform, and time-consuming to instant giving result analysis. In addition to the need for result-driven performances and efficiency in terms of time and resources, there is a growing emphasis on the green aspect and energy efficiency of the analytical sector.

In this regard, solid phase microextraction (SPME), introduced almost 35 years ago, and its headspace mode (HS-SPME) quickly after, shine by their easiness and efficiency to capture and concentrate large varieties of compounds in a solvent-free way prior to their analysis. These features make them one of the most preferred methods in the food analysis sector. However, despite its excellent capabilities, HS-SPME suffers from poor extraction of low-volatile compounds for which increased temperature or longer extraction time may help [1]. However, these conditions can be incompatible with some delicate matrices and analytes, while lengthening the analysis time. Moreover, longer time may exacerbate the displacement effect when relevant [2].

To tackle this issue, several possibilities have been developed over the past decades. One solution is to play adjust the equilibrium conditions by performing extraction under vacuum (Vac-SPME). This allows to decrease the gas-phase resistance to the mass transfer and speeds up the volatilization of low-volatile compounds in the headspace [3]. This concept combined with the ability to trap several extractions before injecting them in a single concentrated analytical shot (Multi-Cumulative trapping, MCT) has been investigated for olive oil and led to an increase of the sensitivity (especially for low-volatile compounds) but also of the obtained information level for cross-sample studies for the same equivalent analysis time [4].

Vac-SPME has been optimized in the present work to quantify 5-hydroxymethylfurfural (5-HMF) by GC×GC-MS in honey and to investigate the possibility of simultaneously analyzing the volatile profile. 5-HMF is a processing contaminant induced by thermal treatment and aging and used as a quality marker. This compound is regulated by the (EU 2001/110/EC) with a maximum limit level of 40 mg/kg and is usually analysed by spectrophotometry after White [AOAC980.23] or Winkler method using Carrez reagents for both, and p-toluidine and barbituric acid for the later or by diluting and then injecting in HPLC [5]. The performance as well as the greenness of the proposed method is compared to the reference HPLC method.

References

[1] Paiva A.C., et al, Trends in Analytical Chemistry, 139, 116252, 2021.
[2] Górecki T., Pawliszyn J., The Analyst, 122 (10), p1079-1086, 1997.
[3] Psillakis E., Anal Chim Acta, 986:12–24., 2017.
[4] Mascrez S., Purcaro G., Anal Chim Acta, 1122:89–96, 2020.
[5] International Honey Commission, Harmonised methods of the International Honey Commission, 2009.

Converting a Moka-Pot into a Green Extraction Tool for the Analysis of Performance Enhancing Drugs via HPLC-MS/MS in Dietary Supplements.

YO-12

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Keywords: *Design of experiments, Dietary supplements, Moka-pot extraction, Performance enhancing drugs, Pressurized solid-liquid extraction.*

In recent years, quick, green and effective extraction strategies became a need in analytical laboratories to support environmental sustainability. Along with the development of more powerful hyphenated instrumental techniques, this led to advanced technologies enabling extremely efficient procedures to be achieved with very low limits of detection. Moka-Pot Extraction (MPE) is a new strategy based on the use of a Moka pot, that consists of three principal aluminium parts: the boiling chamber, which is filled in water; the funnel filter, in which ground coffee is added; and the collecting chamber, where the drink is collected [1]. MPE works at slightly higher pressure than the atmospheric and at high temperatures, and the extraction encompasses two different mechanisms: (i) during the normal phase a solid-liquid extraction occurs, then (ii) the volcanic phase involves a solid-liquid-vapour extraction, thus allowing a higher extraction yield [1]. This consideration led to the conception of the use of a Moka pot as a device for sample preparation for extracting targeted compounds in Dietary Supplements (DS) [2]. DS are widely used worldwide; however, they are often the cause of unintended doping for professional athletes due to the presence of prohibited substances, sometimes not declared in the product information label [3,4]. This study aimed to optimise the extraction efficiency of MPE (including performance enhancing compounds - PECs) and applying the methodology to several DS samples.

As a first proof-of-concept, MPE conditions for the extraction of polar compounds from DS were optimised. A 2^{4-1} fractional factorial design of experiments was implemented, considering the following factors: heating temperature; solvent pH; content of organic modifier (acetonitrile); amount of sample within the funnel filter. The multivariate approach allowed easy determination of the most influential variables (which resulted in the amount of sample, and the interaction between temperature and organic modifier content). From the response surface plots, potentially optimal conditions were suggested [2]. These were firstly validated for 17 target analytes by processing a spiked matrix which did not present any of them, and both the recoveries (between 52 and 134 %) and matrix effects (always negligible or moderate at 100-fold dilution) were calculated from the peak areas obtained after filtration, dilution and analysis. These conditions were applied to real samples: (i) through Hydrophilic Interaction Liquid Chromatography – tandem Mass Spectrometry (MS) 7 of the 17 tested compounds, including artificial sweeteners, methylxanthines and taurine, were detected and quantified [2]; (ii) via a Liquid Chromatography - High Resolution MS analysis the extracts were further screened for more than a hundred PECs.

The obtained concentrations were then compared to those declared on the labels (when available) to check for any possible mislabelling, and to the maximum recommended doses for caffeine and taurine, considering also the daily servings. Interestingly, one DS sample contained caffeine and taurine above the permitted limits [2]. To evaluate the performances of this method, the results were compared with those of a Salt-Assisted Liquid-Liquid Extraction (SALLE) previously developed [5], both in terms of extraction efficiencies and greenness. The two methodologies were quite comparable, even if the MPE was much more efficient in the extraction of taurine, which was not included in the subset of analytes for which SALLE has been optimized [5]. Regarding the greenness, MPE produced higher amounts of waste, but if a smaller Moka was available (e.g. 10 times smaller), it would be even greener than the SALLE [2].

To sum up, this work proved that a Moka-pot, a simple household product, could be used as an effective extraction tool. After the optimization of the method for a few compounds belonging to different classes, the list of targeted analytes was widened, focusing on PECs included in the World Anti-Doping Agency's prohibited list. Thanks to the promising results, the application of such a simple household device could be encouraged, by exploring the extraction of different classes of compounds in other matrices.

References

[1] L. Navarini, E. Nobile, F. Pinto, A. Scheri, F. Suggi-Liverani, Experimental investigation of steam pressure coffee extraction in a stove-top coffee maker, Applied Thermal Engineering 29 (2009) 998–1004.

[2] M. Baglietto, B. Benedetti, M. Di Carro, E. Magi, Assessing the potentialities of an easy-to-use sample treatment strategy: Multivariate investigation on "Moka extraction" of typical ingredients from dietary supplements, Advances in Sample Preparation 10 (2024) 100110.

[3] J.M. Martínez-Sanz, I. Sospedra, C.M. Ortiz, E. Baladía, A. Gil-Izquierdo, R. Ortiz-Moncada, Intended or Unintended Doping? A Review of the Presence of Doping Substances in Dietary Supplements Used in Sports, Nutrients 9 (2017) 1093.

[4] S. Odoardi, E. Castrignanò, S. Martello, M. Chiarotti, S. Strano-Rossi, Determination of anabolic agents in dietary supplements by liquid chromatography-high-resolution mass spectrometry. Food Additives & Contaminants: Part A, 32(5), (2015) 635–647.

[5] M. Baglietto, B. Benedetti, M. Di Carro, E. Magi, Polar licit and illicit ingredients in dietary supplements: chemometric optimization of extraction and HILIC-MS/MS analysis, Anal Bioanal Chem 416 (2024) 1679–1695.

Advantages of the Use of Microwave-Assisted Technology for Lipid Analysis

YO-13

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Keywords: *Microwave-assisted extraction, Food matrices, Bidimensional chromatography*

Since their discovery in 1945, microwaves have gotten increased attention in different fields of applications, including analytical chemistry. When microwave energy is applied, the electric field causes oscillation of the electric dipoles to orient themselves in phase with the electric field that oscillates at a very high frequency, as well as ionic oscillation. These phenomena cause heat production through frictional force. In microwaves, heat is directly applied to the sample, leading to rapid and efficient reaction or extraction of compounds by enhancing the solubility and diffusion, thus requiring lower solvent volume. For these reasons, microwave-assisted processes can be considered more environmentally friendly and cost-effective alternative to classical sample preparation methods, facilitating the transition toward greener and more sustainable analytical chemistry workflows. This presentation aims to highlight the benefits of using microwave-assisted processes, such as extraction and derivatization, in food applications, with a particular focus on lipid analysis. Lipids are fundamental in determining food products' nutritional quality, flavour, texture, and shelf life. Understanding the lipid profile can help in assessing the overall nutritional value of food, including its content of essential fatty acids, cholesterol, and bioactive compounds. Moreover, lipid analysis is critical for quality control and ensuring compliance with food labelling regulations. Nevertheless, analytical methods for lipid analysis are often outdated, tedious, solvent, and time-consuming. Microwave-assisted extraction and/or derivatization can play a fundamental role in modernizing the analytical workflow towards more efficient and greener methods. Several applications will be discussed in which microwaves facilitate improving the efficiency in the quality and safety control in lipid analysis.

Acknowledgments
The authors thank Milestone, Shimadzu and Sepsolve for their support.

Development of Novel Volatile Extraction Method for Raw and Cooked Beef Steak Using High Capacity Sorptive Extraction Thermal Desorption Gas Chromatography Mass Spectrometry

YO-14

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Keywords: *Beef, GCMS, HiSorb, Volatiles*

Flavor comprises of both taste and aroma, with aroma having a much greater impact as it is perceived both ortho- and retro-nasally. The focus of this study was to evaluate and optimize direct immersion high capacity sorptive extraction (DI-HiSorb) thermal desorption (TD) to profile aroma compounds in raw and cooked beef steak by gas chromatography mass spectrometry (GCMS). This study was undertaken on striploin muscle. Different sample preparation conditions were appraised in order to maximize the number of volatile compounds identified. The parameters investigated included (a) sample homogenization, (b) sample amount/solvent (15 % methanol) ratio and (c) different phase HiSorb probes (PDMS vs PDMS/CWR/DVB) (d) on raw and cooked beef steak. Optimal results were achieved using 2g of emulsified beef steak in 13 mL of 15% MeOH, which was prepared by homogenizing equal ratios of finely chopped beef steak with deionized water using an Ultra Turrex dispenser for 2 min in ice, then taking 2g and mixing with 13 mL of 15% MeOH and adding to a 20 mL headspace vial. A PDMS Hi-Sorb probe was directly immersed in the emulsified beef steak MeOH solution at 40°C for 24 hr using a HiSorb agitator. The probes were desorbed pre GCMS analysis using a Centri automated sample extraction platform. Identification of volatiles was undertaken by mass spectral matching from libraries created from standards in association with linear retention indices. All analysis were carried out in triplicate. More than 100 volatile compounds were identified in the raw and cooked beef, which compares very favorably with previous studies [1,2,3]. The impact of internal cooking temperature on the generation of beef volatiles was also evaluated using a clam shell or double sided grill. Raw steak and steaks cooked at five different temperatures: 55°C, 60°C, 71°C, 77°C, 85°C, representing very rare, rare, medium rare, well-done, and very well-done, respectively were evaluated. Analysis was carried out with three experimental and three analytical replicates. These results highlighted the impact of increasing internal steak temperature on the evolution of the volatile profile during cooking. Methyl esters which were more abundant in raw steak and decreased significantly on cooking. Concomitantly, there was a significant increase in other chemical classes such as alcohols, aldehydes, alkanes, benzenes, furans, lactones, and ketones during cooking. Maillard reaction (MR) and thermal oxidation compounds appeared at the highest cooking temperatures, presumably the MR occurred due to a loss of moisture at the contact point between the steak and the hot plate. This study has highlighted the effectiveness of DI-HiSorb TD GCMS to profile volatiles in raw beef steak and to investigate the impact of increasing internal temperature on the volatile profile of beef steak cooked in a double sided grill.

References:

[1] K. Raes, A. Balcaen, P. Dirinck, A. De Winne, E. Claeys, D. Demeyer, S. De Smet, Meat Quality, fatty acid composition and flavor analysis in Belgian retail beef, Meat Sci. 65(4) (2003) 1237–1246.

[2] J.S. Elmore., H.E. Warren., D.S. Mottram., N.D. Scollan., M. Enser., R.I. Richardson., J.D. Wood, A comparison of the aroma volatiles and fatty acid compositions of grilled beef muscle from Aberdeen Angus and Holstein-Friesian steers fed diets based on silage or concentrates, Meat Sci. 68(1) (2004) 27–33.

[3] X. Wang., L, Zhu., Y, Han., L. Xu., J. Jin., Y. Cai., H. Wang, Analysis of volatile compounds between raw and cooked beef by HS-SPME–GC–MS, J. Food Process. Preserv. 42(2) (2018).

New Strategies for the Improvement of the Environmental Impact and Overall Performance of the Sample Preparation for Challenging Fragrance Samples

YO-15

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Keywords: *Aqueous fragrances, Green analytical chemistry, Microextraction techniques, RGB model.*

Analysis of suspected allergenic, cross-contaminant and volatile marker compounds is routinely performed in fragrance quality control laboratories by GC-FID or GC-MS. Conventionally, direct injection of perfume samples is preferred because it is the faster approach and avoids sample preparation steps. However, this method cannot be applied to fragrances with high water content due to unavoidable addition of not volatile cosmetic agents such as solubilizers and emulsifying agents which would require more frequent maintenance of the instrument and could create problems in the chromatographic profile. Conventional sample preparation procedures require a high number of steps and consequently long time procedures, large volume of sample and toxic organic solvents, causing a negative environmental impact.

In this work, innovative and more sustainable sample preparation methods for the analysis of volatile compounds in challenging fragrances with higher amount of water were proposed. Environmental impact of analytical methodologies was taken into account by removing or reducing the amount and the toxicity of extraction materials (sorbent and solvents) and samples used, but also decreasing the sample preparation and analysis time making the extraction process as easy and with lower steps as possible.

Dispersive liquid-liquid extraction technique was miniaturized using a small amount of extraction solvent and sample, and organic solvents were replaced with natural compounds, characterized by simplicity of isolation and preparation and environmental friendliness [1]. Another interesting microextraction approach was based on the use of diatomaceous earth materials (a siliceous sedimentary rock originated from fossilized remains of a type of hard-shelled algae, diatoms), used to absorb water and additives from the samples, followed by the elution of the target analytes using water-immiscible and not toxic solvents [2].

Finally, in order to comprehensively evaluate the developed analytical methods in terms of environmental sustainability, analytical performance and productivity/costs, in this study a metric tool, based on the RGB (Red-Green-Blue) model, was developed and apply to quantitatively measure their overall performance [3].

References

[1] G. Bechis, G. Mastellone, A. Marengo, B. Sgorbini, C. Cagliero, and P. Rubiolo, “Hydrophobic Natural Eutectic Solvents for the Gas Chromatographic Determination of Suspected Allergens in Fragrances by Dispersive Liquid-Liquid Microextraction,” Separations, vol. 9, no. 10, 2022.

[2] R. N. Rao, K. G. Prasad, K. V. S. Kumar, and B. Ramesh, “Diatomaceous earth supported liquid extraction and LC-MS/MS determination of elvitegravir and ritonavir in rat plasma: Application to a pharmacokinetic study,” Anal. Methods, vol. 5, no. 23, pp. 6693–6699, 2013.

[3] G. Bechis et al., “Assessing the environmental and overall performance of gas chromatographic analyses. Development of a comprehensive evaluation framework and application to routine chiral analyses of fragrances as a case study,” Sustain. Chem. Pharm., vol. 35, no. August, p. 101217, 2023.

Synthesis of Sustainable Cyclodextrin-Based Sorbents and Their Application for the Extraction of Organic Contaminants from Environmental Water

YO-16

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Keywords: *Cyclodextrin-based nanosponges, Organic contaminants, Sustainable sorbents, Environmental water*

As recommended by the first principle of Green Analytical Chemistry (GAC) [1], direct analyses should be applied to avoid sample treatment. Nevertheless, in cases of analytes present at trace level and/or interfering compounds, a sample pretreatment is essential and, according to the 3rd criterium of Green Sample Preparation [2], sustainable, reusable, and renewable materials are the most attractive alternative to polymeric sorbents.

For this purpose, harmless, biodegradable, biocompatible, and low-cost sorbents were synthesized using different cyclodextrins (CD). CDs are the natural degradation product of starch, which is one of the most abundant biomasses in the world [3]. They were employed as the monomers, citric acid as the crosslinker and NaH_2PO_4 as the catalyst. The reagents were homogeneously dispersed in the minimum volume of water, and, following a lyophilization step, the polymerization was carried out at 160°C for 2 hours. After the characterization (TGA, IR spectroscopy, and SEM imaging), the obtained biopolymers, called cyclodextrin-nanosponges (CD-NS) due to their morphology, were applied for the dispersive-solid phase extraction of target analytes from river water samples. All the extracts were analyzed by high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) on a cholesteryl analytical column. In line with the 8th principle of GAC (multi-analyte or multi-parameter methods are preferred to methods using one analyte at a time) [1], a wide range of organic contaminants, including pharmaceutical products, pesticides, and hormones, were considered. In particular, after optimizing the best extraction conditions evaluating the sorbent amount, type and volume of elution solvent, the behavior of the different sponges towards the selected analytes was studied in terms of recoveries and reproducibility. Last but not least, recycling tests were performed to evaluate the multiple reuse of such materials studying the variation of extraction yields.

References

[1] Gałuszka, Agnieszka, Zdzisław Migaszewski, and Jacek Namieśnik. "The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices." TrAC Trends in Analytical Chemistry 50 (2013): 78-84.

[2] López-Lorente, Ángela I., et al. "The ten principles of green sample preparation." TrAC Trends in Analytical Chemistry 148 (2022): 116530.

[3] Gentili, Alessandra. "Cyclodextrin-based sorbents for solid phase extraction." Journal of Chromatography A 1609 (2020): 460654.

Development of a New Sorbent Material from Rice Husk Ash for the Preconcentration of Perfluoroalkyl Substances in Environmental Waters

YO-17

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Keywords: *Perfluoroalkyl substances, Rice husk ash, Solid-phase extraction*

Rice husk (RH), a non-food waste biomass, has great potential as a low-cost precursor to produce valuable materials due to its sustainability and environmental friendliness.[1] The main byproduct of its combustion in air is RH Ash (RHA), which has a highly porous structure and can be used as Solid-Phase Extraction (SPE) sorbent for organic pollutants, if opportunely treated.[2] Among these, per- and polyfluoroalkyl substances (PFAS) are anthropogenic chemicals used since the 1950s that have received increased public attention in recent years, due to their toxicity to the environment and humans. The aliphatic fluorinated carbon chain of variable length and a hydrophilic end group, together with the extremely strong C–F bond, confer unique properties to this class of substances such as thermal and chemical stability, resistance to hydrolysis and microbial degradation, leading to their accumulation in the environment.[3] For all these reasons, they are known as 'forever chemicals'.

In this work, a previous synthesis[2] of a sorbent material from RHA was optimized for the preconcentration of 10 PFAS in environmental waters. In particular, the original preparation, which involved 8-hour ultrasound-assisted oxidation in sulfonitric mixture, has been improved moving to 10 minutes of microwave-assisted oxidation with a few millilitres of HNO_3. The expected thermal treatment (10 hours in oven at 200° C) has been optimized by an experimental design evaluating two temperatures (150° C and 250° C) and two times (2 and 10 hours). The four materials obtained, packed in SPE cartridges (250 mg), were tested for sorption capacity in tap water samples (50 mL, native pH) spiked with 1 µg L^{-1} of each PFAS. The best performing material (250° C, 2h) showed quantitative adsorption and elution (by 2 mL MeOH 0.1% v/v NH_3) of the 10 PFAS studied (recovery from 82% to 115%, RSD% < 10%, $n = 3$), analysed by UPLC-ESI-MS/MS with marked internal standards quantification.

The method was then tested in tap water samples spiked with lower environmentally relevant concentrations (100, 50 and 10 ng L^{-1}) with recoveries ranging from 70 to 111% (RSD% < 15%, $n = 3$). The sorbent material is reusable for at least 10 extractions and the sorbent preparation has good repeatability. Tests in river water and wastewater treatment plants effluent at the same concentration levels are ongoing.

Acknowledgements

This research is in the framework of the "PON Ricerca e Innovazione" Ph.D project of Petra Bianchini, DOT1322889-10, D.M. 10-08-21, n° 1061, supported by "Ministero dell'Università e della Ricerca (MUR)" and the European Union. The authors acknowledge the support of MUR and the University of Pavia through the program "Dipartimenti di Eccellenza 2023-2027".

References

[1] M. Ahmaruzzaman, V.K. Gupta, Rice Husk and Its Ash as Low-Cost Adsorbents in Water and Wastewater Treatment, Ind. Eng. Chem. Res. (2011) 50, pp. 13589–13613.
[2] P. Bianchini, F. Merlo, F. Maraschi, R. Brescia, M. Prato, A. Profumo, A. Speltini, From Rice Husk Ash to Silica-supported Carbon Nanomateri-als: Characterization and Analytical Application for Steroid Hormones Pre-concentration from Environmental Waters, Molecules (2023), 28, 745.
[3] K. Miserli, V. Athanasiou, V. Boti, D. Hela, I. Konstantinou, Determination of PFAS in wastewaters and natural waters by solid phase extraction and UHPLC LTQ/Orbitrap MS for assessing occurrence and removals, Case Studies in Chemical and Environmental Engineering 8 (2023) 100505.

Per- and Polyfluoroalkyl Substances Losses in Sample Pretreatment: Sample Preparation, Solid Phase Extraction, Filtration, and ENVI-carb Cleaning

YO-18

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Keywords: *Clean-up, ENVI-carb, PFAS losses, Sample preparation, Solid phase extraction*

Poly- and perfluoroalkyl substances (PFAS) are synthetic compounds characterized by highly fluorinated aliphatic structures comprising a tail and headgroup and have become pervasive in the environment [1]. Given their potential toxic impacts on human health, research into PFAS analysis, fate, and transport in environmental media has garnered significant attention [2]. Conventional PFAS analysis typically involves several steps, including sampling and storage, pretreatment, and instrumental analysis [3]. Pretreatment procedures for solid and liquid samples typically encompass pre-extraction treatment, solid-phase extraction (SPE), clean-up, and drying and re-dissolving processes (Figure 1).

Understanding and minimizing PFAS loss during pretreatment is crucial to ensuring the accuracy of their analysis. For example, PFAS has been proven to be lost by adsorbing to experiment equipment and materials, such as containers and filters. Nonetheless, comprehensive investigations concerning the loss and retrieval of PFAS from commonly used equipment such as centrifuge tubes, SPE cartridges, and ENVI-carb materials are scarce. Consequently, we assessed PFAS losses during sample preparation, SPE, and purification processes, encompassing syringe filter filtration (SFF) and ENVI-carb cleaning, and proposed an enhanced pretreatment method to improve PFAS recovery.

Our assessment revealed significant losses, particularly in long-chain, fluorotelomer sulfonates (FTS), and perfluorooctanesulfonamic acid (FOSAA), during sample preparation and SPE, with higher molecular weights correlating with more substantial losses. Additionally, SFF using regenerated cellulose (RC) filters exhibited an average loss of 50.0% for PFDS (C10) to PFTeDA (C14) and FOSAA. Conversely, no significant PFAS losses occurred during ENVI-carb cleaning when samples were prepared in methanol; however, considerable losses of long-chain species were observed when the solvent comprised 0.5/0.5 water/methanol (v/v). The revised pretreatment method involves utilizing methanol to mitigate adsorption on polypropylene surfaces during sample preparation, thereby enhancing overall PFAS recovery from sample preparation and SPE. Furthermore, washing the RC filter with 6 mL of 0.1% NH_4OH in methanol reduced losses of long-chain and FOSAA by 10.0% to 30.0%. Overall, the modified pretreatment method demonstrated a 20.0% – 50.0% improvement in the recovery of long-chain and FOSAA species.

Crucially, the data obtained suggest that actual concentrations of long-chain (≥ C10) and FOSAA in environmental solid matrices may be significantly higher than those reported in publications. Therefore, the validation of the modified pretreatment approach underscores the importance of gaining insights into PFAS loss during pretreatment and emphasizes the necessity of developing new pretreatment methods specifically tailored for long-chain (≥ C10) and FOSAA species.

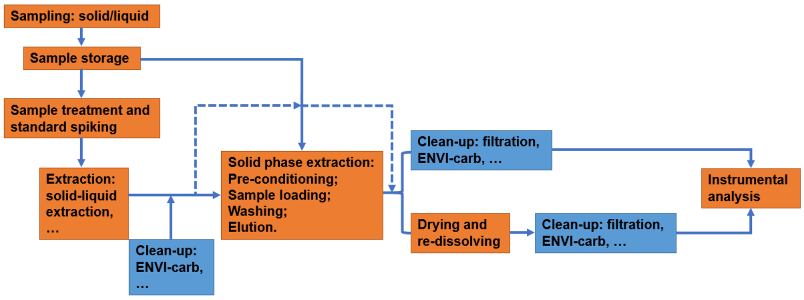

Figure 1. The summarized workflow of PFAS analysis, from sampling to instrumental analysis.

Acknowledgements

This work was financially supported by Horizon 2020, (SENARIOS, 101037509).

References

[1] Buck, Robert C., et al., Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins, Integrated environmental assessment and management 7.4 (2011) 513-541.
[2] Fenton, Suzanne E., et al., Per-and polyfluoroalkyl substance toxicity and human health review: Current state of knowledge and strategies for informing future research, Environmental toxicology and chemistry. 40.3 (2021) 606-630.
[3] Rehman, Abd Ur, Michelle Crimi, and Silvana Andreescu, Current and emerging analytical techniques for the determination of PFAS in environmental samples, Trends in Environmental Analytical Chemistry. 37 (2023) e00198.

Microbeads from Recycled Commercial Polystyrene for the In-Syringe Micro Solid-Phase Extraction of Four Opioids from Environmental and Biological Matrices

YO-19

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Keywords: *Emulsion solidification, In-syringe microextraction, Opioids, Polystyrene recycling*

This communication describes a novel procedure for the extraction and quantitative analysis of four opioids from environmental and biological fluids. The main goal of this study is to introduce an innovative and optimized method for recycling plastic waste, aiming to achieve a consistent and dependable microstructure. The synthesis of a sorbent material from polymeric waste is presented, effectively merging a novel microextraction format with a plastic material recycling process. Polystyrene microbeads, deposited on a rounded piece of paper, have been used as a sorbent material in an in-syringe extraction device. For the preparation of the polymeric device, an already reported **[1]** emulsion solidification technique was optimized, ensuring the achievement of an extremely regular micro material, obtained from second-hand regenerated polymer (yogurt can polystyrene). The retention performance achieved by combining the cellulosic substrate with polystyrene microspheres ensures a broad-spectrum extraction capability across a diverse range of analytes, varying in chemical moieties and polarities **[2]**. The synthetic product is charged directly in the syringe, a frit is used as a support of the rounded paper and as filtration fixture. The sample loading follows the same modality, in a flowthrough mode, by expelling the eluent with the application of a pressure due to a piston. The elution step is carried out with methanol and is performed by keeping the solvent in contact with the polymeric phase for just one minute, collecting the eluent in a vial after the application of a mechanical pressure. The whole analytical procedure is displayed in **Fig. 1**. In this way, the entire device is cheap and user friendly, suitable for the employment in an in-situ analysis, coupling sampling and pre-treatment in the same hyphenated technique. Under the optimum conditions, methadone, tramadol, codeine, and morphine can be determined and quantified by direct injection triple quadrupole mass spectrometry in two different real matrices (swimming pool and saliva), studied as representative substrates for environmental and biological samples, respectively. Limits of detection lower than 8 µg/L and precision better than 14.9% have been obtained for all the analytes in both the considered matrices. The trueness, expressed as relative recovery (RR), ranged from 85% to 114%. In the light of the obtained results, the extraction device has proved to be a valid and sustainable alternative to traditional sorbents, offering good analytical standards and being transversal for the application to different matrices. The simplicity and environmental friendliness of this approach make it highly adaptable across various research and industrial domains.

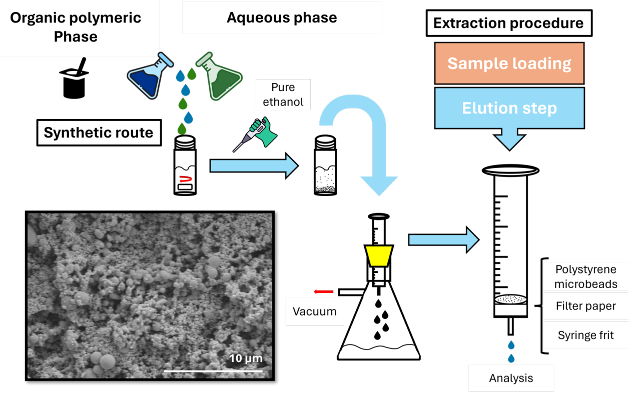

Figure 1. Synthetic route and extraction procedure presented in the current method. SEM image displays the regular and highly reproducible structure of the polymeric microbeads.

Acknowledgements

Financial support from the Spanish Ministry of Science and Innovation (grant PID2020-112868RB) is gratefully acknowledged.

References

[1] Antonelli, L., Frondaroli, M.C., De Cesaris, M.G. et al. Nanocomposite microbeads made of recycled polylactic acid for the magnetic solid phase extraction of xenobiotics from human urine. Microchim Acta 191 (2024) 251.
[2] J. Ríos-Gómez, R. Lucena, S. Cárdenas. Paper supported polystyrene membranes for thin film microextraction, Microchem J 133 (2017) 90-95.

10. Poster Presentations

Biomonitoring of 13 Heavy Metals in Various Types of Leaves from Different Regions of Italy

PSA-01

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Keywords: *Biomonitoring, Heavy metals, ICP-OES*

Pollution of drinking, surface, ground and wastewater with heavy metals is a critical global issue affecting numerous countries worldwide. Heavy metals occur naturally but can also be introduced into the environment through various anthropogenic activities [1]. They are considered as toxic and non-biodegradable chemicals, which can cause health risks [2]. Therefore, effective and reliable heavy metal detection in environment is very important. The greatest risks to human health are caused by arsenic, cadmium, mercury, and lead, while chromium, nickel, cobalt, iron, and manganese are also known to cause harm to human health at elevated concentrations. Various agencies and organizations such as the World Health Organization, European Union, and the US Environmental Protection Agency have established guidelines for heavy metals in water [1]. Biomonitoring concerns the systematic measurement of compounds in living organisms with the purpose of identifying or assessing potential hazardous exposure and effects to chemicals [3]. The leaves of trees can serve as the main indicator of the cleanliness of the environment. In this work we focused on 14 toxic heavy metals (As, Ba, Cd, Cr, Cu, Co, K, Mn, Mo, Ni, Pb, Se, Sr, Zn) in different leaves: leaves from olive tree (*Olea Europaea*), lemon tree (*Citrus Limon*), pomegranate tree (*Punica Granatum*). The aim of the study was to determine the level of heavy metals in olive, lemon and pomegranate leaves from different regions of Italy.

The leave samples were collected from four different regions of Italy: Molise, Campania and Puglia. For digestion we used microwave assisted digestion system Mars 5 (CEM SRL, Cologno Al Serio) at digestion power 600W for 20 min, cooled down for 5 min. Inductively coupled plasma-optical emission spectroscopy 5800 ICP-OES (Agilent Technologies) was employed for the determination of 13 heavy metals: Al, As, Cd, Cr, Cu, Co, Fe, Pb, Mn, Ni, Se, Sb, Zn. The instrumental operating parameters were as follows: 1.2 kW of Rf power, 0.70 L/min of nebulizer gas flow, 12 L/min of plasma – Ar flow, and 1.0 L/ min of auxiliary gas flow. The wavelengths used for quantification were as follows: As – 188.98 nm, Ba – 493.408 nm, Cd – 214.439 nm, Cr – 267.716 nm, Cu – 327.395 nm, Co – 238.892 nm, K – 766.491 nm, Pb – 220.353 nm, Mn – 257.610 nm, Mo – 202.032 nm, Ni – 231.604 nm, Se – 196.026 nm, Sr – 407.771 nm, Zn – 213.857 nm. The samples were prepared by weighing 1 g of the dried leave sample placed directly in the inner vessel. Followed by addition of 20 mL of 65% HNO_3. After digestion, the prepared sample was cooled down to room temperature. The digestion solution was filtered to a 25 mL volumetric flask, the inner wall of the digestion tank was washed with a small amount of deionized water and filled to a final volume of 25 mL.

Biomonitoring is systematic and planned monitoring of air, water and soil quality using living organisms. The result of biomonitoring should be information on the current occurrence of selected species (bioindicators) at individual locations and their mutual comparison not only on the biological but also on the environmental level. As part of method validation, linearity was evaluated, and limits of detection (LODs) and limits of quantifications (LOQs) were calculated. Accuracy of the method in terms of recovery at various concentration levels was determined and precision was expressed using relative standard deviation (RSD). The method was applied for metals quantification in different leaves and from different locations. Chemometric approach was utilized to evaluate data.

In the present study, fourteen elements were quantified in olive, lemon and pomegranate leaves using inductively coupled plasma optical emission spectrometry. Biomonitoring of heavy metals from different plant species and from different geographical locations was approved to be an interesting tool to evaluate the cleanliness of the environment.

Acknowledgements

This work was supported by the call for doctoral students and young researchers of Slovak University of Technology in Bratislava to start a research career (Grant 23-04-05-A). This work was supported by the Slovak Research and Development Agency under Contract No. APVV-19-0149.

References

[1] A. Lace, J. Cleary A Review of Microfluidic Detection Strategies for Heavy Metals in Water, Chemosensors 9 (2021) 60.

[2] E. Aboli, D. Jafari, H. Esmaeili, Heavy metal ions (lead, cobalt, and nickel) biosorption from aqueous solution onto activated carbon prepared from Citrus limetta leaves, Carbon Letters 30 (2020) 638-698.

[3] C. Costa, J.P. Teixeira Biomonitoring, in: P. Wexler (Eds.), Encyclopedia of Toxicology (Third Edition), Academic Press, Bethesda, 2014, pp. 483-484.

Biomimetic Materials and 3D Printing Solid-Phase Microextraction: A Novel Approach to Study Bioaccumulation Factors of Pollutants without the Need of Animal Models

PSA-02

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Keywords: *Biomimetic materials, Biomimetic solid-phase extraction, 3D printing*

Pollutants in the marine environment are persistent substances found in sediments, water, and organisms that can enter the food chain. However, the concentration levels of contaminants are not the only concern regarding these compounds. Bioaccumulation (BA) is an important parameter to consider because it directly affects the food chain and, consequently, human health. The pollutant concentration increases in an organism (mainly in tissues and organs) when it is exposed to a surrounding environment contaminated, being this increase called accumulation. Inside the accumulation field, three important factors can be defined: bioconcentration, bioaccumulation and biota-sediment accumulation factors (BCF, BAF and BSAF, respectively). The most typical parameter studied, due to its easy calculation is BSAF, which is based on the increased chemical concentration in an aquatic organism compared to that in the surrounding sediment. For lipophilic pollutants, sediment concentration is more or less related to all possible exposure routes including dietary absorption, transport across respiratory surfaces and dermal absorption. BSAF can be calculated as the concentration of the pollutant in the organism divided by the concentration of the pollutant in the surrounding sediment. In order to evaluate this parameter, is highly common to determine the concentration of the pollutant directly in the organism, such as bivalves. However, this methodology did not agree with the “3R” principles and REACH recommendations. Therefore, it is important to develop novel methodologies that enable the measurement of this parameters with only *in-vitro* values, using chemometric models that predict the selected bioparameters. However, sometimes it is difficult to mimic all the interactions and the processes that occur in real life. In this sense, the combination of 3D printing to create *ad-hoc* designs and the use of materials with biomimetic interactions could be an interesting alternative. The objective of this work is to develop a biomimetic material, based on phospholipids, integrated into a specialized solid-phase extraction system developed by 3D printing. This system will mimic the interaction of bivalves in their natural environment, enabling the prediction of the BAF parameter for various contaminants. The biomimetic solid-phase extraction (BMSPE) data generated will be used to construct chemometric models, avoiding the necessity to directly measure pollutant concentrations in the selected bivalves. This pioneering approach will mark a significant advancement in the field.

Acknowledgements

The authors acknowledge financial support from the Spanish State Research Agency (AEI//10.13039/501100011033/), the Spanish Ministry of Science, Innovation and Universities (MICIU) and the European Union (NextGenerationEU/PRTR) through projects PID2021-125459OB-I00, PID2020-117686RB-C33 and TED2021-131303B-I00. Also, the authors acknowledge the projects CIGE/2023/069, CIAICO/2022/183 and INVEST/2022/425 funded by Generalitat Valenciana. The authors extend their appreciation to MICINN for granting the Spanish Network of Excellence in Sample preparation (RED2022-134079-T). This communication is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society.

Optimization of a Method Based on MSPD Combined with GC-MS for Determination of Tire Particle Additives in Mussel

PSA-03

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Keywords: *MSPD, Mussel, 6PPD, Tire additives, Tire particles*

Contamination of marine environment by tire particles is an emerging concern. These particles are a great source of microplastic pollution generated after friction of car tires on the roadway during braking or acceleration [1]. Tires are composed of polymeric material and several chemicals added during processing to increase strength and stability of the product. These additives are not covalently linked to polymers, so they are released to marine environment.

The aim of this work is the optimization and validation of a new, rapid, cheap, sensitive and reproducible method based on MSPD (Matrix Sample Phase Dispersion) combined with GC-MS for determination of p-phenylenediamine antioxidants including 6PPD (N-(1,3-dimethylbutyl)- N′-phenyl-p-phenylenediamine), 6PPDq (N-(1,3-Dimethylbutyl)- N′-phenyl-p-phenylenediamine-quinone), DPPD (N, N´-Diphenyl-1,4- phenylenediamine), IPPD (4-Isopropylaminodiphenylamine) and a vulcanization agent BTZ (Benzothiazole) in mussel samples. These family of antiozonants have been found in tire particles [2] and its toxicity in aquatic ecosystems is of great concern [3].

The sample preparation was optimized by using a full orthogonal factorial design 2^^{4} type V+ resolution with two central points (Statgraphics Centurion, Virginia, USA) involving 18 randomized runs. The parameters studied were as follows: amount of Silica as dispersant agent, amount of Florisil as co-column packed, volume of elution solvent, and proportion of the elution solvents (ethyl acetate/dichloromethane). Amounts of sample and sodium sulphate were fixed. Several proofs were performed outside the framework of design to fine tune crucial variables. According to all experiments the optimized MSPD method consisted of 0.5 g of freeze-dried mussel, 0.5 g of anhydrous Na_2SO_4 and 0.5 g of Silica as MSPD mixture, 0.5 g of Florisil as co-column packed and 15 mL of ethyl acetate/dichloromethane 10/90 as elution mixture.

The optimized method was validated in terms of sensitivity (LOQ), accuracy (recovery) and precision (RSD). The limits of quantification (LOQ) of the whole method were calculated as the concentration giving a signal to noise of ten (S/N=10) ranged from 0.18 to 7.8 µg/Kg dry weight. The recovery studies were performed at two levels of concentration 30 and 100 µg/Kg dry weight. Good recoveries were obtained and ranged from 79 to 120 %. The relative standard deviations (RSDs) varied from 2.3 to 14%.

The method was applied to several real mussel samples coming from Galician Rías. BTZ was the compound identified in all studied samples.

Acknowledgements

The authors thank projects PID2022-140148OB-I00, PID2020-117686RB-C32 and RED2022-134079-T (Ministry of Science, Innovation and Universities, Spain), ED431B 2023/04 (Xunta de Galicia). This study is also based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society. All these programs are co-funded by FEDER (UE).

This research was also funded by FEDER/ERDF funds and co-financed by the European Regional Development Fund through the Interreg VI-A Spain-Portugal Programme (POCTEP) 2021-2027 (ref. 0048_BLUE_WWATER_1_E).

References

[1] B. Baensch-Baltruschat, B. Kocher, F. Stock, G. Reifferscheid, Tyre and road wear particles (TRWP) - a review of generation, properties, emissions, human health risk, ecotoxicity, and fate in the environment. Sci. Total Environ. 733 (2020) 137823.

[2] A. Duque-Villaverde, D. Armada, T. Dagnac, M. Llompart, Recycled tire rubber in the Spotlight. Determination of hazardous and lethal substances, Sci. Total Environ. 929 (2024) 172674.

[3] Z. Tian, H. Zhao, K.T. Peter, M. Gonzalez, J. Wetzel, C. Wu, X. Hu, J. Prat, E. Mudrock, R. Hettinger, A.E. Cortina, R.G. Biswas, F.V.C. Kock, R. Soong, A. Jenne, B. Du, F. Hou, H. He, R. Lundeen, A. Gilbreath, R. Sutton, N. Scholz, J. Davis, M. Dodd, A. Simpson, J. McIntyre, E.P. Kolodziej, A ubiquitous tire rubber–derived chemical induces acute mortality in coho salmon, Science 371(6525) (2021) 185-189.

Preparation and Evaluation of 3D-Printed Paddle-Stirrer Coated with Polymers of Different Polarity for the Micro-Solid Phase Extraction of Selected Contaminants from Environmental Water Samples

PSA-04

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Keywords: *3D-printed paddle-stirrers, Environmental waters, Micro-solid phase extraction, Polymers*

In recent decades, human activities have significantly increased the release of chemical pollutants into the environment, many of which are harmful to both the environment and human health even at low concentrations, thus making necessary the development of analytical methods for their determination. In general, a trace enrichment step must be included due to the low concentrations of target contaminants expected in environmental waters. In addition, the wide range of contaminants with different physico-chemical properties poses the challenge of developing methods that effectively and simultaneously address all of them.

Accordingly, in this work, a 3D-printed paddle-stirrer platform for micro-solid phase extraction (µ-SPE) of various environmental pollutants and their subsequent determination by HPLC with ultraviolet (UV) detection is presented. As it is shown in **Figure 1A**, the device consists of 4 paddles assembled to a magnet-containing holder, which allows their rotation while immersed in the water sample using a conventional magnetic stirrer.

The 3D printed paddles were then coated with polymers (**Figure 1B**) of different polarity using different monomers (methacrylic acid and 2-hydroxyethyl methacrylate) and crosslinkers (ethylene glycol dimethylacrylate and divinylbenzene) in different molar ratios. The ability of the different coated paddles to extract three different families of potential contaminants (triazines, sulfonamides and parabens) from water was evaluated. After optimisation of various µ-SPE parameters (washing solvent, elution solvent and pH), the newly developed polymer-coated 3D-printed paddle-stirrer was effectively used to extract target analytes from environmental water samples.

Figure 1. (A) CAD design of the extraction device (paddles and magnet-containing holder) and (B) polymer-coated 3D-printed paddle.

Acknowledgements

The Grant PID2021-122327OB-I00 funded by MCIN/AEI/ 10.13039/501100011033 and by “ERDF A way of making Europe” is gratefully acknowledged. This communication is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society and the National Thematic Network on Sustainable Sample Treatment (RED2022-134079-T) funded by the Spanish Ministry of Science and Innovation.

Paraphenylenediamines and Other Emerging Compounds in Crumb Rubber from Leisure Facilities

PSA-05

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Keywords: *Crumb rubber, Emerging pollutants, Liquid chromatography-mass spectrometry, Tire additives, Ultrasound assisted extraction*

Crumb rubber, obtained from grinding end-of-life tires, is a microplastic material used as infill in artificial turf sports pitches and as playground flooring. The European Commission announced the ban of the use of crumb rubber as infill on September 2023, giving manufacturers 8 years to adapt to this new regulation [1]. Antiozonants, vulcanizers and crosslinking agents are chemical agents present in tires, and consequently, they can appear in this type of surface. Furthermore, they are considered as contaminants of emerging concern for their possible health and environmental negative consequences. Tire wear particles introduce 6PPD-quinone in the aquatic environments, a transformation product of the antiozonant 6PPD (N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine), which is linked to fish mortality [2].

In this research work, an analytical method aiming at determining 11 hazardous chemicals is proposed, including paraphenylenediamines (6PPD and 6PPD-quinone) and other emerging contaminants, such as the vulcanizing and crosslinking agents, 3-di-o-tolylguanidine (DTG), N-cyclohexylbenzothiazole-2-sulfenamide (CBS), and hexamethoxymethylmelamine (HMMM) [3]. The methodology is based on ultrasound assisted extraction followed by liquid chromatography coupled to tandem mass spectrometry (UAE-LC-MS/MS). After optimizing the influence of solvent, temperature, and time of extraction, the method was validated in terms of analytical performance. Finally, it was applied to monitor the target compounds in a wide variety of real crumb rubber samples taken from football pitches, playgrounds, and other urban pavements. Several alternative infill materials, such as sand, cork granulates or thermoplastic elastomers, were also collected and analyzed. All the target analytes were found in the crumb rubber samples. The very high concentration of the antiozonant 6PPD (up to 0.2 % w/w) observed in new synthetic fields should be stressed. Besides, 6PPD-quinone was found in all types of crumb rubber samples, at concentrations up to 40 µg g^{-1} in football pitches. The crosslinking agent HMMM was detected in most of the crumb rubber surfaces, reaching concentrations up to 36 µg g^{-1}. On the other hand, the analysis of the infill alternatives demonstrated these materials were free of the target compounds.

Acknowledgements

This research was supported by projects PID2022-140148OB-I00 and RED2022-134079-T (Ministry of Science, Innovation and Universities, Spain), and ED431B 2023/04 and IN607B 2022/15 (Xunta de Galicia). This study is also based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society. All these programs are co-funded by FEDER (UE).

References

[1] Commission Regulation (EU). 2055 of 25 September 2023 amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) as regards synthetic polymer microparticles. Off. J. Eu. Union L. 238 (2023) 67–88.
[2] Z. Tian, H. Zhao, K.T. Peter, M. Gonzalez, et al., A ubiquitous tire rubber–derived chemical induces acute mortality in coho salmon, Science, 371(6525) (2021) 185-189.
[3] A. Duque-Villaverde, D. Armada, T. Dagnac, M. Llompart, Recycled tire rubber in the Spotlight. Determination of hazardous and lethal substances, Sci. Total Environ. 929 (2024) 172674.

Analysis of 6PPD, 6PPD-quinone and Other Hazardous Chemicals from Tire Rubber in Natural Waters Using Solid-Phase Microextraction

PSA-06

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Keywords: *6PPD, 6PPD-quinone, Gas chromatography - mass spectrometry, Solid-phase microextraction, Tire additives*

During tire manufacturing, many chemicals are added to rubber, and some of them are considered environmental pollutants [1]. These chemicals can enter aquatic ecosystems directly through tire wear particles and indirectly through water leachates from crumb rubber surfaces [2]. The antiozonant 6PPD (N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine) and one of its transformation products, 6PPD-quinone, are linked to the mortality of aquatic species [3]. Vulcanizing and crosslinking agents, such as MBTZ (2-mercaptobenzothiazole) and HMMM (hexamethoxymethylmelamine), are also chemical agents of great interest because of their potential impact on the environment and human health [4,5].

The aim of this work is the development of an analytical methodology for the detection and quantification of emerging contaminants from tire rubber in water. This methodology is based on solid-phase microextraction (SPME) followed by gas chromatography coupled to tandem mass spectrometry (GC-MS/MS). Several parameters affecting the SPME step were optimized to achieve an efficient methodology for all the analytes. An experimental design evaluating the extraction mode, temperature, fibre coating and salting out effect was carried out. Moreover, extraction time and pH were also evaluated in this work. Then, the methodology was validated in analytical terms. In order to assess the transfer of the target analytes between the rubber material and the water in contact with it, crumb rubber samples were placed in contact with natural waters for 24 h. Subsequently, the water was collected and analyzed. Finally, the methodology was applied to real water samples collected from playgrounds, football fields, and parking places. Some of the target analytes, including 6PPD, 6PPDq and HMMM, were found in the real waters demonstrating their leaching from the rubber.

Acknowledgements

This research was supported by projects PID2022-140148OB-I00 and RED2022-134079-T (Ministry of Science, Innovation and Universities, Spain), and ED431B 2023/04 and IN607B 2022/15 (Xunta de Galicia). This study is also based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society. All these programs are co-funded by FEDER (UE). A.D.V. appreciates the help of the excellence grant from EuSP2024|GSAC2024.

References

[1] A. Duque-Villaverde, D. Armada, T. Dagnac, M. Llompart, Recycled tire rubber in the Spotlight. Determination of hazardous and lethal substances, Sci. Total Environ. 929 (2024) 172674.

[2] M. Celeiro, D. Armada, N. Ratola, T. Dagnac, J. de Boer, M. Llompart, Evaluation of chemicals of environmental concern in crumb rubber and water leachates from several types of synthetic turf football pitches, Chemosphere 270 (2021) 128610.

[3] Z. Tian, H. Zhao, K. T. Peter, M. Gonzalez, et al., A ubiquitous tire rubber–derived chemical induces acute mortality in coho salmon, Science 371(6525) (2021) 185-189**.**

[4] C. Johannessen, P. Helm, C.D. Metcalfe, Detection of selected tire wear compounds in urban receiving waters, Environ. Pollut. 287 (2021) 117659.

[5] K. Müller, D. Hübner, S. Huppertsberg, T.P. Knepper, D. Zahn, Probing the chemical complexity of tires: Identification of potential tire-borne water contaminantswith high-resolution mass spectrometry, Sci. Total Environ. 802 (2022) 149799.

Pipette-Tip Membrane Microextraction for the Determination of Antibiotics in Natural Waters

PSA-07

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Keywords: *Antibiotics, Polymer inclusion membranes, Water*

A new microextraction method using a polymer inclusion membrane (PIM) in a pipette tip is proposed for the extraction of the antibiotics sulfathiazole (STZ), sulfamethazine (SMZ), and sulfamethoxazole (SMX) prior HPLC detection. These antibiotics can be found in aquatic systems due to their widespread uses.

The optimization of the key parameters affecting the PIM extraction and elution was previously studied by immersion extraction methodology, using a 3 cm^2 membrane area of different composition, and 100 mL of antibiotics at 100 µg L^{-1} concentration in mineral water. It was found that PIMs made of either cellulose triacetate (CTA) or poly(vinyl) chloride (PVC) as polymers with the ionic liquids trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) or methyltrioctylammonium chloride (Aliquat 336), resulted in effective sorbents for the extraction of the three antibiotics at a neutral pH and 24 h contact. The elution was achieved using 1 mL MeOH in vortex agitation. Moreover, the effect of membrane aging was investigated using a PIM made of 50%PVC-50%Cyphos IL 101. Extraction/elution experiments were conducted using three different PIMs: one prepared recently, one prepared 3 months ago, and one prepared 1 year ago. The results demonstrated no differences in the recovery of STZ, SMZ, and SMX when using either the recently prepared PIM or the 3-month-old membrane. However, the efficiency decreased when using the 1-year-old PIM. This study highlights that the extraction phase can be stored, without any special care, for at least 3 months before use.

With the aim of combining the excellent sorption characteristics of the PIM with a quicker methodology, we incorporated the membrane into a pipette tip. Several parameters were studied, including those which can affect extraction efficiencies, such as the PIM composition and the volumes and number of extraction/elution cycles of the sample and eluent. The linear range of this method was between 0.2 and 2 mg L^{-1} each compound for 10 aspirating cycles for the extraction and 5 cycles for elution (20 s each). The matrix effect was investigated using spiked samples of tap water, mineral water and a river water and acceptable recovery values were obtained.

Acknowledgements

This work has been supported through the project PID2022-140312NB-C22 funded by MICIU/AEI/10.13039/501100011033/ FEDER, UE.

Automated High-Capacity Sorptive Extraction of Volatile Per- and Polyfluoroalkyl Substances (PFAS) from Drinking Water

PSA-08

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Keywords: *Contaminants, Environmental, PFAS, Water*

PFAS (per- and polyfluoroalkyl substances) are a group of man-made chemicals known for their water- and grease-resistant properties, widely used in various industrial and consumer products. After a national sampling of tap water in homes across the US by the United States Geological Survey (USGS) it is now estimated that 45% of drinking water is contaminated with PFAS compounds, ranging from 0.35 to 350 ng/L.[1] The large range of concentrations across three orders of magnitude and low reporting limits, which are suggested to be 0.1 µg/L for 20 individual PFAS and 0.5 µg/l for the total PFAS concentration, make the already difficult analysis of PFAS even more challenging.[2]

There is currently an analytical gap for volatile PFAS compounds which are not readily detectable via HPLC - the standard method for analyzing PFAS from aqueous samples – but are more GC-amenable. [2] These specific compounds (e.g., Fluorotelomer alcohols (FTOH), perfluorooctane sulfonamido ethanols (FOSE), perfluorooctane sulfonamides (FOSA)) are extremely mobile and becoming progressively abundant due to the increase of remediation processes for PFAS compounds thus creating these more volatile PFAS compounds as a result.

The flexibility of the Centri platform was used to investigate automated high-capacity sorptive extraction techniques to preconcentrate low-levels of these PFASs from water. After extraction the analytes are transferred to a multi-bed, backflushed focusing trap for further preconcentration, to reach the challenging limits of detection mandated, prior to GC injection. While the detection limits for FTOHs in water were often reported in the high parts per trillion (ppt) to low parts per billion (ppb) range, by combining sorptive extraction with trap-based preconcentration we successfully achieved these lower limits of detection.

Additionally, in comparison to LC-based methods, sample preparation was minimised and more green. Preconcentration by re-usable sorptive extraction devices removed the need for single-use consumables, such as SPE cartridges, and eliminated harmful solvents and their costly disposal. Water samples were placed directly into 20 mL headspace vials and onto the autosampler for analysis.

References

[1] Shoemaker, J. AND Dan Tettenhorst. Method 537.1 Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS).

[2] DIRECTIVE (EU) 2020/2184 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 2020 on the quality of water intended for human consumption.

Dispersive Solid-Phase Extraction Using Alginate/Graphene Oxide Composite Gel Beads for Preconcentration of Heavy Metals in Environmental Water Samples

PSA-09

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Keywords: *Alginate, Gel beads, Graphene oxide, Heavy metals, Solid-phase extraction*

In recent years, graphene oxide (GO) and related carbonaceous nanomaterials have attracted great interest in environmental applications. Their large surface area, abundance of carboxyl, epoxy and hydroxyl groups on the surface and edges, as well as water dispersibility make them a good sorbent for solid-phase extraction (SPE) of various analytes. However, the separation of GO from the aqueous solutions after adsorption tends to be quite difficult. A possible option to overcome separation related issues is the use of composites based on biopolymers. Alginate (Alg) is a non-toxic biopolymer rich in hydroxyl and carboxyl groups distributed along its backbone chain. The incorporation of GO into alginate gel beads offers ease of separation, thus enabling the application of Alg/GO composite gel beads as sorbents in dispersive SPE (DSPE). In addition, biopolymer-based sorbents are considered as green and environmentally friendly materials due to their non-toxicity, biocompatibility and biodegradability, so the investigation of their possible application in SPE analytical procedures is of great importance.

In this study, DSPE method based on composite Alg/GO gel beads was employed for the simultaneous extraction and preconcentration of toxic heavy metal ions (zinc, cadmium, lead and copper) from water samples and combined with differential pulse anodic stripping voltammetry (DPASV) for analyte determination at trace levels. A Metrohm 797 VA Computrace polarography system based on the reference method No. 231/2e (Application Bulletin) was used for all voltammetric measurements. DPASV conditions are as follows: drop size, 4; purge time, 300 s; deposition potential, -1.15 V; deposition time, 60 s; equilibration time, 10 s; start potential, -1.15 V; end potential, 0.01 V. The volume of the preconcentrated sample solution introduced in the voltammetric cell was 100 µL.

The GO content within the prepared composite beads was 0.1 wt% (**Figure 1**). Identification of Alg/GO surface functionalities was conducted by Fourier Transform Infrared Spectroscopy (FTIR). Parameters influencing extraction and preconcentration of heavy metals including amount of adsorbent, extraction time, sample volume and desorption conditions were investigated and optimized. In order to optimize conditions of DSPE procedure and obtain high recoveries of selected metals, the extractions were conducted in a conical plastic tubes by adding 0.1 – 0.5 g of wet Alg/GO beads in a series of 50 mL aqueous sample solutions spiked with 1 mg/L of each metal (pH 5.5). The mixtures were stirred for 60 min at 200 rpm to allow the analytes to be adsorbed onto the Alg/GO beads. After that, the beads were separated from the aqueous solutions, rinsed with deionized water and subjected to vortex-assisted desorption step. The recovered heavy metal mixture containing Pb(II), Cu(II), Cd(II) and Zn(II) ions was analyzed by DPASV. The recovery, R (%), of each metal was calculated as R = (C_f/C_0)*100, where C_f and C_0 are the final and initial concentration of particular heavy metal ion.

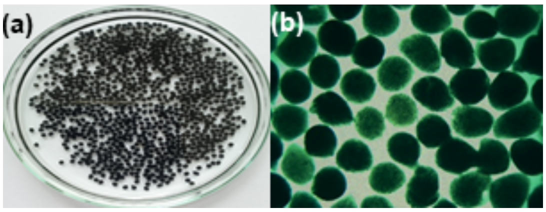

Figure 1. (a) Photograph and (b) optical microscopy image of alginate/GO beads.

The results on the effect of amount of Alg/GO beads showed that the recovery of metals increased up to 75%, depending on particular ion, with increase of the sorbent mass from 0.1 to 0.4 g and then remained constant. Based on these results, the Alg/GO mass of 0.4 g was selected as the optimal in extraction procedures. DSPE was further optimized by studying the effect of shaking time on the extraction of metal ions, indicating that 45 min is optimum extraction time needed to achieve the equilibrium conditions between the Alg/GO beads and sample solution containing selected metal ions. The highest recoveries (> 70%) for all metal ions were obtained by desorption with 3 mL of 2 M HNO_3. Under the optimized conditions, the proposed Alg/GO DSPE method exhibited good linearity in the range of 10 – 500 µg/L for Cu(II), Pb(II), Cd(II) ions and in the range of 25 – 500 µg/L for Zn(II) ions, with the determination coefficients between 0.991 and 0.995. The limits of detection (LODs) were 0.005, 0.004, 0.007 and 0.018 mg/L for Pb(II), Cu(II), Cd(II) and Zn(II) ions, respectively. The developed Alg(GO DSPE method was also applied to the determination of trace heavy metals in environmental water samples with satisfactory results.

Acknowledgements
We acknowledge the support to this work provided by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia through contract number 451-03-66/2024-03/200017.

Photodegradation Studies of Tire Rubber Additives in Water Using Solid-Phase Microextraction

PSA-10

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Keywords: *Emerging pollutants, Gas chromatography - mass spectrometry, Photodegradation, Solid-phase microextraction, Tire additives*

Pollution by microplastics is one of the priority issues of various organizations and agencies, including the European Chemicals Agency (ECHA) [1]. Concern about the use of microplastics from tire recycling (crumb rubber) in sports and gaming facilities is also one of ECHAS's 12 hot topics [2]. Tire rubber contains a complex mixture of chemical substances in its composition to improve its properties. Because of tire wear, these compounds are introduced into the environment, generating a great threat due to their high toxicity even at low concentrations. Among them, the antiozonant 6PPD (N-(1,3-dimethylbutyl)-N′-phenyl- p-phenylenediamine) and one of its transformation products, 6PPD-quinone, have been recently linked to the death to aquatic species [3]. One of the main environmental degradation processes and purification treatment processes for contaminated waters is photodegradation. Many chemicals are susceptible to phototransformation since their structures contain chromophore groups that absorb light at wavelengths in the UV and visible regions of the spectrum. The main objective of this work is to investigate the photochemical behavior of antiozonants, vulcanizing agents and other tire chemical contaminants in water, including 6PPD and 6PPDq. The photodegradation is carried out employing UV light. Degradation kinetics are studied, and the results are compared with the ones for the degradation in different environmental water matrixes (rainwater, irrigation water, seawater, …). Also, the influence of pH in the photodegradation process has been studied. For the detection and quantification of the target compounds, an already optimized and validated solid-phase microextraction methodology followed by gas chromatography coupled to tandem mass spectrometry has been employed (SPME-GC-MS/MS). Furthermore, photo-SPME was also carried out to follow the degradation kinetics of the target compounds [4]. The transformation of 6PPD into the toxic 6PPD-quinone was observed.

Acknowledgements

This research was supported by projects PID2022-140148OB-I00 and RED2022-134079-T (Ministry of Science, Innovation and Universities, Spain), and ED431B 2023/04 and IN607B 2022/15 (Xunta de Galicia). This study is also based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society. All these programs are co-funded by FEDER (UE). A.D.V. appreciates the help of the excellence grant from EuSP2024|GSAC2024.

References

[1] ECHA (European Chemical Agency). Microplastics, https://echa.europa.eu/hot-topics/microplastics.

[2] ECHA (European Chemical Agency). Granules mulches on pitches playgrounds, https://echa.europa.eu/hot-topics/granules-mulches-on-pitches-playgrounds.

[3] Z. Tian, H. Zhao, K.T. Peter, M. Gonzalez, et al., A ubiquitous tire rubber–derived chemical induces acute mortality in coho salmon, Science, 371(6525) (2021) 185-189**.**

[4] L. Sánchez-Prado, M. Llompart, M. Lores, et al., Further research on the photo-SPME of triclosan. Analytical and bioanalytical chemistry, 384 (2006) 1548-1557.

$Fe_3O_4/SiO_2/TiO_2$ Nanocomposite for Magnetic Solid-Phase Extraction of Pharmaceuticals: Sorption and Desorption Study with MIP Application

PSA-11

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Keywords: *Magnetic silica/titanium core–shell nanocomposite, Magnetic solid-phase extraction, Molecularly imprinted polymer, Pharmaceuticals*

The constant entry of pharmaceuticals into the environment as a result of increasing production and consumption poses a great danger to living beings exposed to these substances, which are invisible to the eye. The protection of the environment and the establishment of regulations require the continuous development of sensitive and reliable analytical methods for the detection and removal of these emerging pollutants from different media. Depending on the type of sample (soil, water, biota and sediment), different extraction techniques and materials are used as sorbents that can remove pharmaceuticals of different polarity. In this research, magnetic solid-phase extraction was tested using core–shell $Fe_3O_4/SiO_2/TiO_2$ nanocomposites as sorbents. The nanocomposite was prepared by microwave-assisted synthesis described in the previously published paper with the attached characterization of the material [1]. The extraction of thirteen pharmaceuticals with different physicochemical properties was demonstrated by studying the sorption and desorption performance of the above-mentioned particles. The influence of various parameters on the extraction yield, such as sorption kinetics, pH, initial concentration of pollutants, sorbent dosage, temperature, ionic strength, type and volume of elution solvent and desorption time, were determined. Therefore, the optimized magnetic solid-phase extraction showed the best performance by describing the sorption kinetics with the pseudo-second order model, with the contact of 1 mg/L pollutants mixture (at pH 6) without ionic strength (0 M NaCl) and 20 mg nanocomposite during 1 h at 25 °C, and desorption/elution with 5 mL methanol by three extraction step (1+2+2) within 15 min. To increase the selectivity of the method and enable better sorption of sulfametoxazole (SMETOX), a molecularly imprinted polymer (MIP) was prepared. SMETOX as a template molecule was imprinted on a $Fe_3O_4/SiO_2/TiO_2$ nanocomposite, and the experiment was repeated under the same optimal extraction conditions. It is expected that the prepared MIP nanocomposite will have a greater specificity towards SMETOX, therefore the method itself will be more selective for the determination of SMETOX in a mixture with other drugs, which is very often case in practice. The samples were monitored using the HPLC-DAD gradient method.

Acknowledgements
This study was supported by the Croatian Science Foundation under the project number HRZZ-IP-2022-10-4400 entitled Development of molecularly imprinted polymers for use in analysis of pharmaceuticals and during advanced water treatment processes (MIPdePharma).

References

[1] I. Gabelica, L. Ćurković, V. Mandić, I. Panžić, D. Ljubas, K. Zadro, Rapid microwave-assisted synthesis of $Fe_3O_4/SiO_2/TiO_2$ core-2-layer-shell nanocomposite for photocatalytic degradation of ciprofloxacin, Catalysts 11 (2021) 1136.

Capsule Phase Microextraction Combined with Gas Chromatography-Tandem Mass Spectrometry for the Determination of Polychlorinated Biphenyls in Water Samples

PSA-12

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Keywords: *Capsule phase microextraction, GC-MS/MS, Polychlorinated biphenyls, Water samples*

Polychlorinated biphenyls (PCBs) are synthetic organic compounds that are used in a wide range of industrial and commercial applications. Due to the adverse effects of these compounds on human health and ecosystems, their careful monitoring is necessary. In this work, a capsule phase microextraction (CPME) protocol was developed for the extraction of eight PCBs (i.e., 2-chlorodiphenyl, 2,3-dichlorobiphenyl, 2,4,5-trichlorobiphenyl, 2,2',4,4'-tetrachlorobiphenyl, 2,2',3',4,6-pentachlorobiphenyl, 2,2',4,4',5,6'-hexachlorobiphenyl, 2,2',3,3',4,4',6-heptachlorobiphenyl, 2,2',3,3',4,5,6,6'-octachlorobiphenyl) from water samples prior to their determination by gas chromatography-tandem mass spectrometry (GC-MS/MS). In CPME, the microextraction device is made of two permeable microporous polypropylene tubes welded together. One polypropylene tube contains a sol–gel hybrid organic–inorganic sorbent, while the other contains a cylindrical magnet. Thus, the extraction device integrates the stirring and filtration mechanisms [1]. The main parameters that affect the adsorption and desorption steps (i.e., type of capsule, sample volume, extraction time, stirring rate, ionic strength, type and volume of eluent, and desorption time) were studied. The sol-gel Carbowax 20 M encapsulated microextraction capsules were found to be the optimum for the extraction of PCBs. The extraction was achieved within 20 min under constant stirring at 100 rpm using 20 mL of sample. The elution was performed by immersing the capsule in 500 μL of acetone for 5 min. Accordingly, the CPME-GC-MS/MS method was validated in terms of linearity, sensitivity, selectivity, enhancement factor, accuracy, and precision. Good linearity, selectivity, sensitivity, accuracy, and precision. The applicability and the green character of the proposed method were also evaluated using Blue Applicability Grade Index and Complementary Green Analytical Procedure Index. Finally, the novel method was successfully employed for the analysis of environmental water samples.

References

[1] A. Ferracane, N. Manousi, A. Kabir, K.G. Furton, P.Q. Tranchida, G.A. Zachariadis, J. Plotka-Wasylka, L. Mondello, V.F. Samanidou, E. Rosenberg, Monolithic capsule phase microextraction prior to gas chromatography-mass spectrometry for the determination of organochlorine pesticides in environmental water samples, Microchemical Journal, 186 (2023) 108355.

Ultrasound-Assisted Emulsification Microextraction (USAEME) for the Sensitive Determination of Different Chemical Class Herbicides in Water

PSA-13

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Keywords: *Microextraction techniques, Ultrasound-assisted emulsification micro-extraction (USAEME), Herbicides, Environmental waters, Chromatography, Mass spectrometry*

The rising global population and the increasing demand for agricultural raw materials, both for human and animal consumption, makes the agrifood sector crucial for any nation. In the coming decades, agriculture's foremost challenge will be still to satisfy the escalating global food demand while ensuring environmental sustainability. Achieving this goal implies the development of sustainable agricultural and farming methods, which includes the use of pesticides that may pose significant health risks (e.g., carcinogenicity, mutagenicity, reproductive toxicity) and environmental hazards (e.g., toxicity to aquatic life with long-lasting effects) [1]. Once applied to crops and soils [2], pesticides undergo various physico-chemical processes, such as degradation, transformation, photolysis, sorption-desorption, and leaching. A primary cause of ground and surface water contamination by pesticides is the migration of active substances through the soil, influenced by soil characteristics, meteorological conditions, and the chemical properties of the compounds [3].

This study focuses on herbicides mainly used for to maize crops, featuring diverse characteristics, including two low-dose sulfonyurea herbicides (rimsulfuron and nicosulfuron), a biopesticide (spinosad), a highly utilized and rapidly degraded aromatic ketone herbicide (mesotrione), and a chiral imidazoline herbicide (imazamox).

The aim of this research was to develop a sensitive analytical methodology to identify and quantify the selected herbicides in surface water, followed by their accurate determination in agricultural soils. For this purpose, ultrasound-assisted emulsification microextraction (USAEME) was chosen to extract the target analytes from water. Various influential factors such as pH, salt addition, extraction time, and extraction solvent were investigated and optimized using experimental design. After establishing the optimal extraction conditions, the method was validated and applied to real environmental water samples. The analyses were performed using liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) in selected reaction monitoring (SRM) mode. The first results revealed the high sensitivity and robustness of the method, reaching concentrations at the low ng L^{-1} for 5 of the target analytes, including metolachlor, pendimethalin, prosulfuron, dimethenamid and terbuthylazine in environmental water samples. Future studies will focus on the extraction and analysis of the targeted herbicides in soil cores collected between 10 and 30 cm of depth in agricultural plots.

Acknowledgements

The authors thank projects PID2022-139874OR-C22, and RED2022-134079-T (Ministry of Science, Innovation and Universities, Spain), ED431B 2023/04 and IN607B 2022/15 (Xunta de Galicia). This study is also based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society. All these programs are co-funded by FEDER (UE). S.S.O would like to thank to Ministry of Science, Innovation and Universities for its predoctoral contract (PREP2022-000520). A.C.L acknowledges Xunta de Galicia for its predoctoral contract (ED481A and IN606A).

References

[1] J.P. Bourdineaud. Drug and Chemical Toxicology. 45(2) (2022) 698-721.
[2] A. Castiñeira-Landeira, L. Vazquez, H. Gonzalez-Leirado, M. Llompart, T. Dagnac. 415(29) (2023) 7197-7209.
[3] I. Chopra, B. Kumari, S.K. Sharma. Environmental monitoring and assessment. 160 (2010) 123-126.

Sorption Performance of Molecularly Imprinted Polymer for the Selective Extraction of Sulfamethoxazole

PSA-14

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Keywords: *Molecularly imprinted polymer, Sorption isotherms, Sorption kinetics, Sulfamethoxazole*

Sulfametoxazole (SMETOX) is a sulfonamide antibiotic that is mainly used in human and veterinary medicine. It is characterized as a persistent molecule that is detected together with other poorly degradable pharmaceuticals in various environmental areas such as wastewater, surface water, groundwater, soil, etc. To improve the selectivity of detection methods for SMETOX in this research and in general for other pollutants present in the environment in microgram and nanogram quantities, molecularly imprinted polymers are prepared as extraction sorbents. Sulfametoxazole as template molecule was molecularly imprinted by bulk polymerization using methacrylic acid as monomer, ethylene glycol dimethacrylate (EDGMA) as crosslinker and azobisisobutironitril (AIBN) as initiator (molar ratios = 1 : 4 : 20). The capacity of MIP was determined by batch sorption experiments in which the binding kinetics, the influence of pH, initial concentration, temperature, sorbent dosage, and ionic strength were tested and the selectivity of material was compared with the sorption capacity of NIP (non-imprinted polymer). The amount of sorbed SMETOX on the tested polymer materials was determined by HPLC-DAD analysis. In terms of kinetics, the sorption equilibrium between SMETOX and MIP/NIP was reached after about 24 hours, and the nature of sorption was best described by a pseudo-second order model, with an emphasis on better sorption using imprinted material. The sorption affinity of the pharmaceutical towards MIP and NIP was described by few isotherm models ($R^2 > 0.9$), where different sorption parameters were estimated.

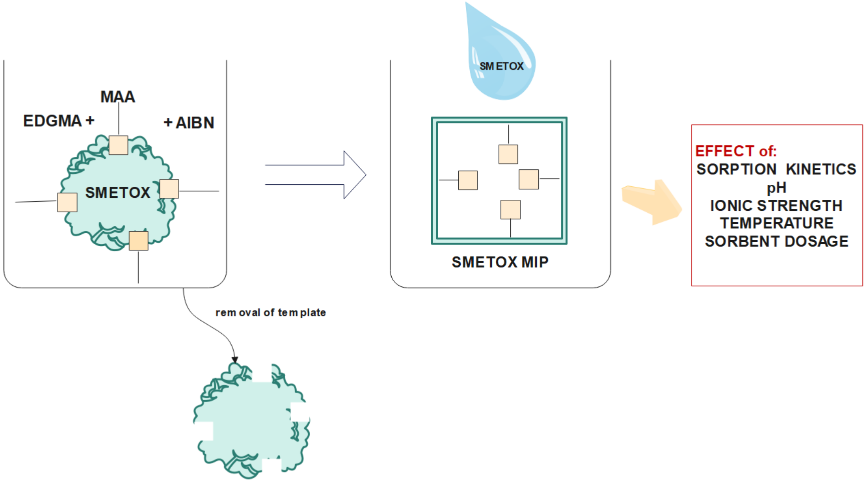

Figure 1. Shematic representation of MIP sorption experiments.

Acknowledgements
This study was supported by the Croatian Science Foundation under the project number HRZZ-IP-2022-10-4400 entitled Development of molecularly imprinted polymers for use in analysis of pharmaceuticals and during advanced water treatment processes (MIPdePharma).

Fabric Phase Extraction Empowered by the Use of Molecularly Imprinted Polymers for the Highly Selective Isolation of BPA from Water Samples Analyzed by HPLC-DAD

PSA-15

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Keywords: *Bisphenol A, Fabric phase sorptive extraction, HPLC-DAD, Microextraction, Molecularly imprinted polymers*

Bisphenol A (BPA) is a ubiquitous industrial chemical used in the production of polycarbonate plastics and epoxy resins, found in numerous consumer products such as food and beverage containers, thermal paper receipts, and medical devices. Due to its widespread use and potential adverse health effects, including endocrine disruption and reproductive toxicity, the determination of BPA has become paramount in environmental and public health research. This study introduces an advanced green analytical method for the determination of Bisphenol A (BPA) using Fabric Phase Sorptive Extraction (FPSE) combined with Molecular Imprinted Polymers (MIPs), followed by High-Performance Liquid Chromatography with diode array detection (HPLC-DAD). The MIP-FPSE leverages biodegradable solvents and minimizes reagent consumption, aligning with green chemistry principles. The optimization involved the systematic investigation of the key parameters that affect the performance of the MIP-FPSE procedure, including pH adjustment, absorption time, desorption solvent, volume of desorption, stirring time, stirring ratios, elution time, and salt effect [1]. Optimum parameters were identified as follows: extraction was carried out within 20 min under a stirring rate of 300 rpm, the optimum desorption solvent consisted of 1 mL of a mixture of acetonitrile and methanol (50:50, v/v), and elution was carried out within 30 s. The proposed method was validated and the limit of quantification (LOQ) was determined at 25 μg mL^{-1}. The developed method exhibited excellent precision, with relative standard deviation (RSD%) for intra and inter-day precision not exceeding 7% and 15%, respectively. The analytical method demonstrated a linear response over the concentration range of 0.025 -10 μg mL^{-1}, with a coefficient of determination (R^2) of 0.999. Accuracy, expressed as recovery rates, ranged between 91.3% and 97.1%. The total analysis time was 4.2 minutes, using isocratic elution with mobile phases consisting of acetonitrile (ACN) and water (H_2O) in a 70:30, v/v ratio. This green sample preparation approach, coupled with HPLC-DAD, provides a reliable, accurate, and precise method for BPA detection across aqueous samples. The integration of MIP-FPSE with HPLC-DAD underscores the feasibility and effectiveness of sustainable analytical practices in environmental and health-related research.

References

[1] P. Kubica, N.P. Kalogiouri, A. Kabir, K.G. Furton, V.F. Samanidou, Optimization of a Fabric Phase Sorptive Extraction protocol for the isolation of six bisphenols from juice pouches to be analysed by high performance liquid chromatography coupled with diode array detector, J. Chromatogr. A 1708 (2023) 464366.

A Magnet-Integrated Fabric Phase Sorptive Extraction Protocol as a Front-End to GC-MS/MS for the Trace Determination of Polycyclic Aromatic Hydrocarbons in Water Samples

PSA-16

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Keywords: *Fabric phase sorptive extraction, GC-MS/MS, Microextraction, Polycyclic aromatic hydrocarbons, Water samples*

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds composed of two or more fused benzene rings. Due to their carcinogenicity and mutagenicity, many PAHs are dangerous to human health. Consequently, PAHs are considered as priority pollutants by the US Environmental Protection Agency (EPA) and the European Environmental Agency. PAHs often exist at trace levels in water samples, and thus their determination must be conducted using analytical methods with high selectivity and sensitivity. In this work, a magnet-integrated fabric phase sorptive extraction (MI-FPSE) protocol was developed for the extraction of 16 PAHs from water samples prior to their determination by gas chromatography-tandem mass spectrometry (GC-MS/MS). In MI-FPSE, two FPSE membranes are sandwiched together, and a metallic magnetic stirrer is integrated into the extraction device, providing an “all-in-one” extraction device with enhanced extraction kinetics [1]. The main parameters that affect the performance of the MI-FPSE procedure (i.e., type of sol-gel sorbent, sample volume, extraction time, stirring rate, ionic strength, type and volume of eluent, desorption time) were studied. Sol-gel poly(tetrahydrofuran) MI-FPSE media provided the highest extraction efficiency. The extraction was achieved within 40 min under constant stirring at 1000 rpm. The optimum sample amount was 50 mL and its ionic strength was adjusted using 20% m/v NaCl. The elution of the retained analytes was achieved within 2 min using 500 μL of acetone. Following their optimization, the analytical method was validated in terms of linearity, sensitivity, selectivity, enhancement factor, accuracy, and precision. The developed method showed good linearity, accuracy, and precision. The limits of quantification for the target analytes were down to 10 pg L^{-1}. Good linearity, selectivity, as well as intra-day and inter-day accuracy and precision were observed. The applicability and the green character of the proposed method were also evaluated, and the MI-FPSE-GC-MS/MS method was successfully employed for the analysis of drinking water samples.

References

[1] N. Manousi, V. Alampanos, A. Ferracane, G. Efstratiadis, A. Kabir, K.G. Furton, P.Q. Tranchida, G.A. Zachariadis, L. Mondello, E. Rosenberg, V.F. Samanidou, Magnet integrated fabric phase sorptive extraction as a stand-alone extraction device for the monitoring of benzoyl urea insecticides in water samples by HPLC-DAD, Journal of Chromatography A, 1672 (2022) 463026.

Extraction of Phenolic Compounds from Olive Pomace Using Supramolecular Deep Eutectic Solvent

PSA-17

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Keywords: *β-cyclodextrin, HPLC-MS, Phenolic compounds, Supramolecular deep eutectic solvent*

The large quantities of waste produced by the agri-food chain are critical factors for industries, as they represent high management and disposal costs. A valid solution to this problem is their reuse: from the waste it is possible to extract molecules, such as phenolic compounds, that can be reused in other industries, such as pharmaceuticals, nutraceuticals or food industries. Therefore, this sustainable approach allows waste to have a second life, in accordance with the principles of the circular economy [1]. Phenolic compounds can be found in many plant matrices: in fact, these produce secondary metabolites, which have a beneficial effect on human health. Due to their antioxidant power, phenolic compounds are able to prevent the onset of inflammatory and neurodegenerative diseases. For this reason, there has recently been a growing interest in this class of molecules and their extraction from vegetable matrices [2]. In accordance with green chemistry principles, the extraction procedure used should respect the basis of sustainability. Conventional organic solvents, such as methanol, acetone, and hexane, are not suitable for this purpose, and for this reason they are being replaced by green solvents such as water and ethanol. These, due to their nature, are compatible and considered non-toxic for humans. Despite this, interest in innovative and sustainable solvents, such as Deep Eutectic Solvents (DESs), has increased in recent years. These solvents have now been widely studied in the literature and used for the extraction of phenolic compounds from many food matrices and supply chain wastes [3]. Recently, DESs have also been evaluated as extraction solvent with the addition of β-cyclodextrins. These are cyclic oligosaccharide molecules obtained from the degradation of starch due to the activity of some enzymes, and are characterized by seven glucose units, with a central cavity that interacts selectively with the analytes of interest through non-covalent bonds. Their chemical and physical characteristics allow them to be selective toward certain molecules, such as phenolic compounds. These innovative solvents, called Supramolecular Deep Eutectic Solvents (SupraDESs), seem to be excellent green solvents against the extraction of phenolic compounds and are a sustainable alternative to conventional ones [4]. The aim of this project was to develop and optimize an analytical procedure for the extraction of phenolic compounds from the olive pomace, using a SupraDES composed by ammonium acetate - lactic acid (in a ratio of 1:7) with the addition of a certain amount of β-cyclodextrin. Specifically, the extraction procedure initially involved the optimization of the concentration of β-cyclodextrins to be added to DES (0.7, 1.8, 2.1, 4.5 % w/w). Then an one-factor-at-a-time optimization was used to define levels of the factors to be subsequentially optimize using a statistical Box-Behnken Design method. Specifically three factors at three levels were considered to develop Box-Behnken design: extraction temperature (20, 35 and 50 °C), extraction time (10, 20 and 30 minutes) and ratio of matrix quantity to solvent volume (1:20, 1:35 and 1:50 w/v). The optimized extraction procedure consists on the best extraction time of 22 minutes, temperature of 43 °C, solid-liquid ratio of 1:48 (g:mL) and β-cyclodextrins concentration of 1.8 % (w/w). Finally, the scalability of the method was carried out by increasing the quantity of matrices and the volume of solvent, keeping the ratio constant, in order to evaluate the efficiency of solvent extraction. Moreover, the Complementary Green Analytical Procedure Index (ComplexGAPI) highlighted the sustainable nature of the extractive solvent. The extraction method based on the use of SupraDES allowed an increase in the extraction yield compared to the use of DES without β-cyclodextrins and conventional organic solvents. Finally, the qualitative profile of the extracted phenolic compounds was performed using an High Performance Liquid Chromatography coupled to a Mass Spectrometer.

References

[1] A. Mir-Cerdà, O. Nuñez, M. Granados, S. Sentellas, J. Saurina, An overview of the extraction and characterization of bioactive phenolic compounds from agri-food waste within the framework of circular bioeconomy, TrAC, Trends Anal. Chem. 161 (2023).
[2] L. Panzella, F. Moccia, R. Nasti, S. Marzorati, L. Verotta, A. Napolitano, Bioactive Phenolic Compounds From Agri-Food Wastes: An Update on Green and Sustainable Extraction Methodologies, Front. Nutr. 7 (2020) 60.
[3] J. Werner, A. Zgola-Grześkowiak, J. Platkiewicz, J. Plotka-Wasylka, N. Jatkowska, A. Kalyniukova, S. Zaruba, V. Andruch, Deep eutectic solvents in analytical sample preconcentration Part B: Solid-phase (micro)extraction, Microchem. J. 191 (2023).
[4] R. Cai, Y. Yuan, L. Cui, Z. Wang, T. Yue, Cyclodextrin-assisted extraction of phenolic compounds: Current research and future prospects, Trends Food Sci. 79 (2018) 19-27.

β-cyclodextrin and Levulinic Acid Based Supramolecular Deep Eutectic Solvent: Characterization and Applications for the Extraction of Bioactive Molecules

PSA-18

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Keywords: *β-cyclodextrin, Bioactive molecules, Levulinic acid, HPLC-PDA, SUPRADES*

In recent years, the main engine of analytical chemistry is to move towards increasingly green and sustainable applications and, for this reason, green chemistry strives to identify alternative and environmentally friendly conditions [1].

A recent discovery that could be a breakthrough in the context of green chemistry are supramolecular deep eutectic solvents (SUPRADESs), a new subclass of deep eutectic solvents (DESs).

Just like DESs, SUPRADESs consist of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA); the difference between the latter is that HBA is made up of cyclodextrins. Cyclodextrins (CDs) are non-toxic cyclic oligosaccharides derived from the enzymatic degradation of starch [2].

Native CDs consist of six (α-CD), seven (β-CD) or eight (γ-CD) α-(1 → 4) linked D-glucopyranose units and are characterized by a hydrophobic internal cavity and hydrophilic external surface that allow to encapsulate hydrophobic and volatile compounds [3].

The ability of DESs to bind numerous compounds through the formation of hydrogen bonds is further enhanced by the presence of cyclodextrins, which interact with them through guest-host inclusion complexes.

CDs have attracted interest for a wide range of applications including food, agrochemicals, environmental chemistry, catalysis, cosmetics and pharmaceuticals [4].

The aim of this work, was to synthesize, characterize and evaluate SUPRADESs as innovative sustainable solvent for phenolic compounds extraction performance. In particular, the SUPRADES used was composed of native CDs which behaved as HBA and levulinic acid that behaved as HBD according to a specific molar ratio (1:27). The mixture was then stirred at 60 °C until a clear homogeneous liquid was obtained and then cooled to room temperature. Since CDs have many HBA sites (from 35 sites for native β-CD and 35 to 55 sites for modified β-CD), a large molar excess of levulinic acid was used.

A β-CD SUPRADES characterization study was performed using Fourier-transform infrared spectroscopy (FTIR) and an ATR analysis confirmed the structure of the SUPRADES. The frequencies of the bonds present in the SUPRADES were compared with those of the corresponding individual components, β-CD and levulinic acid, respectively.

Preliminary tests were carried out to evaluate the extractive capacity of SUPRADES towards bioactive molecules, such as phenolic compounds.

Specifically, methanolic solutions of single standard molecules (ferulic acid, gallic acid and syringic acid) were placed in contact with different quantities of SUPRADES for different contact times using a vortex. Subsequently, the percentage recovery of phenolic compounds within SUPRADES was assessed.

SUPRADESs have proved to be promising new solvents with an excellent affinity towards bioactive molecules and represent a green alternative to traditional organic solvents, approaching the requirements of "green chemistry".

For the best of our knowledge, the present work represents the first attempt to use this innovative and promising levulinic acid based supramolecular solvent for phenolic compounds recovery.

Acknowledgements

The activities were performed within Project ECS 0000024 Rome Technopole, - CUP B83C22002820006, NRP Mission 4 Component 2 Investment 1.5, Funded by the European Union – NextGenerationEU.

References

[1] A.M. Wanisa, A.Q. Ali, A.O. Errayes, Green chemistry: principles, applications, and disadvantages, Chem. Methodol. 4 (2020), 408-423.
[2] Crin, G. Review: a history of cyclodextrins, Chem Rev, 114(21) (2014) 10940-75.
[3] M. Kfoury, L. Auezova, H. Greige-Gerges, S. Fourmentin, Encapsulation in cyclodextrins to widen the applications of essential oils, Environ. Chem. Lett. 17 (2019) 129–143.
[4] G. Crini, S. Fourmentin, É. Fenyvesi, G. Torri, M. Fourmentin, N. Morin-Crini, Cyclodextrins, from molecules to applications, Environ. Chem 16 (2018) 1361–1375.

β-Cyclodextrins-Coated Magnetic Nanoparticles: Synthesis, Characterization, and Adsorption Studies

PSA-19

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Keywords: *Adsorption, β-Cyclodextrins, Host–guest interaction, Magnetic nanoparticles, Magnetic solid phase extraction*

In the recent years, iron oxide magnetic nanoparticles (MNPs) have attracted considerable attention, due to their high saturation magnetization and simple production process [1]. MNPs are of great interest for researchers from a wide range of disciplines, including biotechnology/biomedicine, magnetic resonance imaging, synthesis of magnetic fluids, and environmental remediation [1]. In published works, MNPs are used in various applications, such as in drug delivery as drug carriers, or in biomedical applications for the determination of different xenobiotics from biological samples [1].

MNPs are often coated with different materials and used in a variety of ways. In this work, a cyclodextrins (CDs)-based coating was considered to achieve the goal of preparing a sustainable material. CDs are cyclic oligosaccharides obtained from the enzymatic degradation of starch, composed of optically active D-glucopyranose units linked through α-(1,4)-glycosidic bonds [2]. In particular, β-CDs were chosen, characterized by the presence of seven monosaccharide units and internal diameter of 0.78 nm [2].

A preliminary study for the synthesis, characterization and use of these magnetic materials was performed.

With the aim of evaluating the possible water remediation application of these MNPs and the characteristic host-guest interactions of CDs, some preliminary tests were performed, using analytes with a simple structure. Since compounds with para-disubstituted aromatic rings are known to penetrate the CD cavity better, 4-aminobenzoic acid, 4-chlorobenzoic acid, 4-nitrophenol, and terephthalic acid were considered. Magnetic solid phase extraction (MSPE) of analytes was possible thanks to the magnetic nature of the material and the external coating.

Several synthetic strategies were proposed. For the first synthesis, a reaction intermediate obtained by Hasan et al. [3] was exploited. Initially, magnetite was synthesized from a co-precipitation method using $FeSO_4$ and $FeCl_3$ in a basic environment [4]. A magnetite quantity of 1.0 g was added to a 12 mM aqueous solution of β-CDs. The resulting solution was magnetically stirred for 4 hours at room temperature and a series of washes with ethanol were performed to remove β-CD excess.

A further synthesis procedure involved modifying a method found in the literature [4] by using a bridging molecule between the β-CDs and the magnetite core. Once the magnetite was prepared, 5 mL of pure reagent (ethylenediamine or ethylene glycol) and 1.81 g of β-CDs were added. The solution was magnetically stirred for about 30 minutes at 80°C. A series of washes with water and ethanol were performed to remove the unreacted β-CDs and the base excess until a neutral pH was reached. Finally, all the MNPs prepared were dried in an oven at 60°C overnight.

A characterization study using Fourier-transform infrared spectroscopy (FTIR) made it possible to verify the actual presence of β-CDs on the magnetic core.

The contact between a certain quantity of MNPs and a composite standard solution in water of the aforementioned analytes was performed and studied. Subsequently, the resulting solution was vortexed, and the MNPs were removed simply by means of an external magnet. The injection of the liquid phase, left after contact with MNPs, in a high-performance liquid chromatography (HPLC) system coupled with a photodiode array (PDA) detector showed a clear decrease in analyte concentrations. Among all the tested MNPs, the analyte adsorption by β-CDs-ethylene glycol-coated MNPs was found to be the best.

Once the type of MNP that ensured the highest percentage removal of analytes was selected, parameters such as MNPs-to-solution volume ratio, contact time, and possible extraction media (vortex or ultrasonic bath) were optimized. Subsequent analyte desorption from MNPs was also investigated.

The synthesized material adequately responds to some of the most important principles of Green Sample Preparation (GSP) [5]. In fact, the new material is synthesized using “safer solvents and reagents” (2nd principle), minimizing waste generation (4th principle) and the amounts and volumes of “sample, chemicals and materials” (5th principle). Finally, its use makes it possible to reduce the extraction procedure energy consumption (8th principle), since the material can be easily moved by an external magnet. In the future, it is planned to apply the material for water remediation evaluations or determination of pesticides from food or biological samples.

References

[1] A.H. Lu, E.E. Salabas, F. Schüth, Magnetic nanoparticles: synthesis, protection, functionalization, and application, Angew. Chem. Int. Ed. 46 (2007) 1222-1244.

[2] Y. Li, F. Liu, T. Abdiryim, X. Liu, Cyclodextrin-derived materials: From design to promising applications in water treatment, Coord. Chem. Rev. 502 (2024) 215613-215643.

[3] K. Hasan, I.A. Shehadi, R.G. Joseph, S.P. Patole, A. Elgamouz, β-Cyclodextrin-Functionalized Fe_3O_4-Supported Pd-Nanocatalyst for the Reduction of Nitroarenes in Water at Mild Conditions, ACS Omega 8 (2023) 23901−23912.

[4] R. Shelat, S. Chandra, A. Khanna, Detailed toxicity evaluation of β-cyclodextrin coated iron oxide nanoparticles for biomedical applications, Int. J. Biol. Macromol. 110 (2018) 357-365.

[5] Á.I. López-Lorente, F. Pena-Pereira, S. Pedersen-Bjergaard, V.G. Zuin, S.A. Ozkan, E. Psillakis, The ten principles of green sample preparation, TrAC Trends in Analytical Chemistry 148 (2022) 116530-116539.

The Solvent-Assisted Dispersive Solid-Phase Extraction for Determination of Anionic Surfactant with UV-Vis Detection

PSA-20

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Keywords: *Microextraction, SA-DSPE, Surfactants*

The solvent-assisted dispersive solid-phase extraction (SA-DSPE) [1] is a miniaturized technique of the solid-phase extraction for separation and preconcentration of analytes. In this technique, a sorbent is injected into a liquid sample as a solution miscible with water solvent. The SA-DSPE technique is similar to DLLME [2] and has similar advantages, for example, it uses small amounts of sorbent and lacks the disadvantage of the "memory" effect. This technique has also a bottleneck in the phase separation step. It was found that the sorbent, after extraction and centrifugation, tended to float at the aqueous phase surface and was lost when the aqueous phase was withdrawing. In this work, the problem of sorbent loosing was solved through the formation of an oversaturated solution of sorbent at the moment of injection of sorbent solution into the sample solution.

To illustrate the workability of the suggested approach the SA-DSPE method for determination of anionic surfactants (AS) was developed. The method is based on the formation of ionic associate (IA) between astrafloxin (cationic dye) and AS in an acidic medium with subsequent extraction of the formed IA with benzophenone. Benzophenone (as a 5% solution) was injected into the system as its solution in the dispersion solvent - acetone. The formed dispersion of benzophenone was separated from the aqueous phase by centrifugation and the formed sediment was recrystallized by adding a few crystals of the benzophenone. The supernatant was easily decanted. The resulting precipitate was dissolved with 500 μL of acetone and absorbance measurements were carried out in a semi-microcuvette. A calibration plot was linear in the range up to 0.5 μmol L^{-1} of Na-dodecylbenzenesulfonate (Na-DBS). The limit of detection (LOD) and limit of quantification (LOQ) were 9.0 and 30 nmol L^{-1} of Na-DBS, respectively.

Acknowledgements
Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V01-00043. Authors would like to express their thank to the Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic (VEGA 1/0220/21) for financial support.

References

[1] M.R. Jamall, A. Firouzjah, R. Rahnama, Solvent-assisted dispersive solid phase extraction, Talanta 116 (2013) 454-459.
[2] M. Rezaee, et al., Determination of organic compounds in water using dispersive liquid–liquid microextraction, Journal of Chromatography A 1116(1-2) (2006) 1-9.

Vial-Coated Thin Film Microextraction for Perfluorinated Carboxylic Acids (PFCAs) Determination in Water Samples by GC-MS

PSA-21

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Keywords: *Gas chromatography-mass spectrometry, Perfluorinated compounds, Sample preparation, Solid phase microextraction, Thin film microextraction*

Within perfluoroalkyl substances (PFAS), perfluorocarboxylic acids (PFCAS) stand out as one of the most studied subgroups due to their bioaccumulative nature. Exposure to PFCAs is linked to hepatotoxicity, cancer, and adverse effects on human development. For these reasons, PFCAS are environmental contaminants of concern, and due to their low pKa values, prevail in aquatic environments [1]. Liquid chromatography-tandem mass spectrometry (LC-MS/MS) and solid-phase extraction (SPE) are commonly reported techniques for PFCAS determination. However, when using SPE, a prior filtration step is necessary, and, it has been reported that PFAS can adsorb to filtration membranes, causing analyte loss [2,3]. Additionally, contamination issues with PFAS may arise due to the presence of its precursor, fluorotelomer alcohol 8:2 in LC-MS/MS systems [4]. In contrast, gas chromatography-mass spectrometry (GC-MS) is a more cost-effective technique, commonly used, despite the need for sample derivatization. Regarding sample pretreatment, solid phase micro extraction simplifies and accelerates the analysis procedure, avoiding the clogging of the packed resin when working with complex matrices.

As a result, considering the complexity of PFAS sample pretreatment a thin-film micro extraction (TFME)-coated device for sample extraction process was designed, using GC-MS for PFCAS (C5-C10) determination. Glass was selected as the support material, due to its low adsorption rate and chemical resistance, compared to polypropylene and other polymers [3]. TFME coating was created using weak anionic exchange resin and polyacrylonitrile as a binder polymer (10% w/w) because it is capable of extracting analytes in complex matrices, without the co-extraction of proteins and macromolecules as interferents [5]. The proposed method avoids filtering the sample, thereby preventing the loss of PFCAS in the filtration membrane prior to extraction. Under optimal conditions, the extraction efficiency of the developed method was in the range of 70 - 100%. The method limits of detection and quantification ranged from 0.13 - 2.1 ng L^{-1} and 0.42 – 7.1 ng L^{-1}, respectively. The intra-and inter-assay coefficients of variation were 4.87 – 2.15% and 4.74 - 2.33%, respectively, and the linear working range for TFME- coated device was 10 – 1000 ng L^{-1}. Therefore, the proposed method can be employed for the determination of PFCAS in drinking water, meeting the requirements of the Directive 2020/2184 (maximum allowable limit of 0.5 μg L^{-1} for total PFAS).

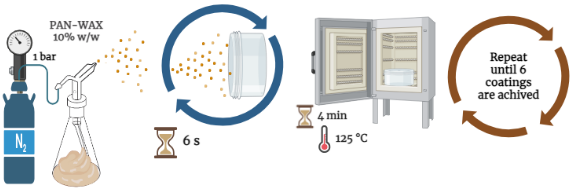

Figure 1. Coating procedure of the vial with TFME.

Acknowledgements

Financial support from the Spanish Ministry of Science and Innovation, Agencia Estatal de investigación (project PID2019-107604RB-I00/MCIN/AEI/ 10.13039/501100011033) is gratefully acknowledged. J. Mabel Luna gratefully acknowledges the National Council of Humanities, Sciences and Technologies (CONAHCYT) and Environment and Energy Department, Advanced Materials Research Center (CIMAV) S.C in Mexico for the pre-doctoral research fellowship.

References

[1] S.P. Lenka, M. Kah, L.P. Padhye, A review of the occurrence, transformation, and removal of poly- and perfluoroalkyl substances (PFAS) in wastewater treatment plants, Water Res 199 (2021) 117187.
[2] M. Sörengård, V. Franke, R. Tröger, L. Ahrens, Losses of poly- and perfluoroalkyl substances to syringe filter materials, J Chromatogr A 1609 (2020).
[3] S.P. Lenka, M. Kah, L.P. Padhye, Losses of Ultrashort- and Short-Chain PFAS to Polypropylene Materials, ACS ES and T Water 3 (2023) 2700–2706.
[4] R.A. Brase, E.J. Mullin, D.C. Spink, Legacy and Emerging Per- and Polyfluoroalkyl Substances: Analytical Techniques, Environmental Fate, and Health Effects, Int J Mol Sci 22 (2021) 1–30.
[5] F.S. Mirnaghi, Y. Chen, L.M. Sidisky, J. Pawliszyn, Optimization of the coating procedure for a high-throughput 96-blade solid phase microextraction system coupled with LC-MS/MS for analysis of complex samples, Anal Chem 83 (2011) 6018–6025.

Modern Trends in Pre-Analysis in Clinical Research and Routine Practice

PSA-22

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Keywords: *Dry blood spot, Immune activation markers, Pipette tip extraction, UHPLC-MS/MS, Vitamins*

Advanced sample preparation is one of the most important tools of modern laboratory medicine. Techniques that focus on patient safety and convenience, simplicity, and speed of analysis are the key goals of newly developed methods. For many years we have been developing methods based on such techniques, which are now used and tested in many clinical studies. Only a good practical method can be applied to patient samples in clinical studies, the number of which is currently increasing [1]. The situation is similar in routine practice. The combination of selective and sensitive separation techniques with the modem trends of pre-analysis is very advantageous in many cases and allows its increasing integration in laboratory medicine.

We are interested in the determination of liposoluble vitamins and markers of immune system activation (neopterin, kynurenine, and tryptophan) in various biological fluids. All methods that will be presented have been developed in our laboratory and applied to a variety of clinical studies [2,3,4,5].

Modern trends we are interested in are especially microsampling techniques based on dry blood spots and dry urine spots. Their main advantages are simplicity, patient protection, easy transport and storage of samples, and simple processing. We work with modern commercially available microfluidic devices such as Capitainer® and Hemaxis® and also test new nanofibrous polymers with properties designed for the specific application.

Another modern trend is to make sample preparation as simple as possible, often based on only a few easy steps such as precipitation and filtration. These steps are usually carried out in microtiter plates that require small sample volumes. We are also engaged in usage of pipette tips for extraction. We tested a variety of approaches including SPE, SALLE, and phospholipid binding [6].

All our preanalytical approaches are combined with modern UHPLC-FLD/PDA/MS/MS methods using columns containing different stationary phases such as core-shell particles, sub-2 µm particles, and monoliths.

will demonstrate each of the aforementioned trends with our results in pre-analysis, separation techniques, and some of the clinical studies that we have performed [7].

Acknowledgements

This work was supported by project SVV 260 662 and by the University Hospital in Hradec Králové MH CZ DRO (UHHK, 00179906), Charles University grant GAUK 121124. Authors also acknowledge the Ministry of Health projects NU22-01-00151, NU21J-02-00021, and NW24-05-00031 All rights reserved.

References

[1] L. Kujovska Krcmova, B. Melichar, F. Svec, Chromatographic methods development for clinical practice: requirements and limitations, Clin. Chem. Lab. Med. 58 (2020) 1785-1793.

[2] K. Mrstna, K. Matousova, L. Kujovska Krcmova, A. Carazo, J. Pourova, P. Mladenka, L. Matysova, L., F. Svec, Analysis of vitamin K1 and major K2 variants in rat/human serum and lipoprotein fractions by a rapid, simple, and sensitive UHPLC-MS/MS method, J. Chromatogr. A 1714 (2024) 464548.

[3] K. Mrstna, D. Turonova, Ch. Suwanvecho, F. Svec, L. Kujovska Krcmova, The power of modern extraction techniques: A breakthrough in vitamin K extraction from human serum, Microchem. J. 198 (2024) 110170.

[4] A. Vernerova, L. Kujovska Krcmova, O. Heneberk, V. Radochova, O. Strouhal, A. Kasparovsky, B. Melichar, F. Svec, Chromatographic method for the determination of inflammatory biomarkers and uric acid in human saliva, Talanta 233 (2021) 122598.

[5] J. Plisek, L. Kujovska Krcmova, J. Aufartova, T.V. Morales, S.M Esponda, R. Oros, E. Kasalova, J.J. Santana Rodriguez, L. Sobotka, P. Solich, D. Solichova, New approach for the clinical monitoring of 25-hydroxyvitamin D-3 and 25-hydroxyvitamin D-2 by ultra high performance liquid chromatography with MS/MS based on the standard reference material 972, J. Sep. Sci. 36 (2013) 3702-3708.

[6] Ch. Suwanvecho, L. Kujovska Krcmova, F. Svec, Effective, convenient, and green sample preparation for the determination of retinol and retinol acetate in human serum using pipette tip microextraction, Talanta 262 (2023).

[7] L. Kujovska Krcmova, L. Javorska, K. Matousova, P. Smahel, M. Skala, M. Kopecky, Ch. Suwanvecho, N. Privratska, D. Turonova, B. Melichar, Evaluation of inflammatory biomarkers and vitamins in hospitalized patients with SARS-CoV-2 infection and post-COVID syndrome, Clin. Chem. Lab. Med. 62 (2024).

Preconcentration of Bromide and Bromate by In-Vessel Headspace Liquid-Phase Microextraction Followed by Their Spectrophotometric Determination

PSA-23

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Keywords: *Bromate, Bromide, In-vessel headspace liquid-phase microextraction, Spectrophotometry*

We have recently proposed a new microextraction (ME) technique called headspace liquid phase microextraction (IV-HS-LPME) [1]. The proposed approach is fully compatible with conventional microcuvettes and instruments used in spectrophotometry. Placing the acceptor phase in a specially designed vessel inside a sealed vial completely eliminates previous problems with microdrop stability, limitations on stirring speed or extraction time, and, above all, the volume of the acceptor phase.

Since almost any volume of extractable phase can be placed in the vessel, the proposed approach can in principle be combined with many other analytical techniques such as luminescence, flame AAS or liquid chromatography. Importantly, the proposed approach is not inferior to methods using a microsyringe to retain the extraction solvent in terms of extraction efficiency. At the same time, the advantages of the HS mode, such as free choice of solvent including aqueous solutions, complete separation from matrix components, and absence of memory effect, are retained.

The conditions for preconcentration by IV-HS-LPME method and spectrophotometric determination of bromide were found, using its transformation into volatile elemental bromine by reaction with excess chloramine T. Bromine was absorbed by 50 µL of 1% potassium iodide solution placed in an extraction vessel. The absorbance of the resulting triiodide complex solution was measured in a 1 cm microcuvette at 350 nm. Optimal values of reagent concentrations were as follows: chloramine T – 0.03 mM, sulfuric acid – 0.5 M, extraction time – 45 min, magnetic stirrer rotation speed – 800 rpm. The developed method has a sensitivity of 0.08 µM or 10 ppb, which allows controlling the concentration of bromides in all types of natural waters.

Conditions were found for bromate preconcentration by IV-HS-LPME method and subsequent spectrophotometric determination using conversion of bromate to volatile elemental iodide by reaction with excess iodide. Iodine was absorbed by 50 µL of 1% KI solution in the acceptor phase. The following parameters of bromate determination were optimized: iodide concentration – 0.09 mM, sulfuric acid concentration – 0.01 mM, extraction time – 30 min, magnetic stirrer rotation speed – 1000 rpm. The developed method has a sensitivity of 0.02 µM or 2.5 ppb, which allows controlling it at the level of existing requirements ($C < 10$ ppb). The developed methods have been successfully applied for determination of bromide and bromate content in natural and drinking waters.

Acknowledgements
Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V01-00106 (Andrii Vyshnikin).

References

[1] A.-E. Tamen, A. Vishnikin, In-vessel headspace liquid-phase microextraction, Anal. Chim. Acta 1172 (2021) 338670.

Untargeted Metabolomics for Monitoring *Sinularia* Soft Coral Response to Elevated Sea Temperature

PSA-24

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Keywords: *Climate change, Environmental metabolomics, Molecular networking, Soft corals*

Coral reef communities have been long viewed as one of the most treasured ecosystems. Despite the ecological and economic value of such assemblages, the increasing anthropogenic activities ranging from climate change over pollution to diseases pose a great threat to them. Interestingly, the Red Sea accommodates the most thermo-tolerant corals which warrants the need of exploring their underlying mechanisms of resilience [1]. Soft corals are one of the influential members that governs the complexity of the reef ecosystem, the molecular basis of their response is ambiguous to the increasing temperatures associated with global climate change [2], necessitating the need for further investigations. The identification of the key metabolic biomarkers of the coral outcome(s) to various environmental stresses could offer valuable insights into the reaction and hence adaptability of soft corals to ecological pressures, particularly the rising water temperatures.

Sinularia species are among the most widespread soft corals. In our study, we aimed to identify the key metabolic biomarkers of different *Sinularia* sp. in response to elevated sea water temperatures. *Sinularia* samples were collected from different locations along the Egyptian Red Sea coast with varying sea water temperatures, to comparatively explore their metabolic profile through recruiting environmental metabolomics. For this untargeted ultra-performance liquid chromatography coupled to high resolution tandem mass spectrometry (UPLC-HRMSMS) was the chosen analytical protocol with the aid of molecular networking.

Analysis of the acquired mass spectrometry analysis revealed the existence of betonicine (proline derivative) and trigonelline in *Sinularia* samples collected from Marsa Allam with water temperatures peak in the range 28 to 30°C, *versus* nicotinamide, and niacin in Hurghada samples with sea temperature ranging from 22 to 28°C. Considering the secondary metabolome, nonsignificant difference was observed in the distribution of the detected chemical classes, albeit some variation of individual metabolites was observed. Further studies are needed to uncover the ecological significance of the detected metabolites and to elucidate their potential contributing mechanisms to the soft corals resilience to rising sea water temperatures associated with the global climate change.

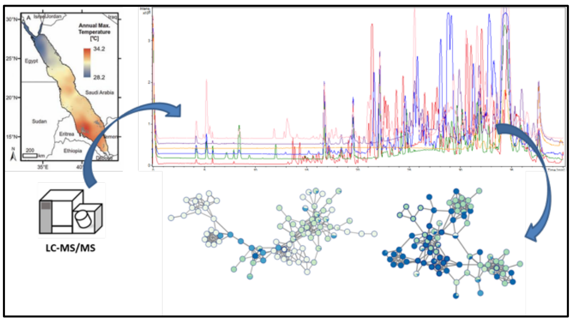

Figure 1. Scheme of work.

References

[1] M. Fine, et al., Coral reefs of the Red Sea—Challenges and potential solutions, Reg. St. Mar. Scie. 25 (2019) 100498.
[2] D.G. Maucieri, J.K. Baum, Impacts of heat stress on soft corals, an overlooked and highly vulnerable component of coral reef ecosystems, at a central equatorial Pacific atoll, Bio. Conservation 262 (2021) 109328.

Optimized Liquid-Liquid Extraction Method for the Determination of Buprenorphine and its Main Metabolite in Commercial Plasma Using HPLC-UV

PSA-25

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Keywords: *Buprenorphine, Liquid chromatography, Liquid liquid extraction, Norbuprenorphine, Opiod dependence*

Opioid use disorder (OUD) is characterized by a lifelong struggle to control drug consumption, representing a chronic and recurrent disease. Despite the effectiveness of pharmacotherapies like methadone, buprenorphine/naloxone, and naltrexone, cravings often persist, resulting in continued illicit opioid use and contributing to the low treatment engagement, with only 20-40% of diagnosed individuals receiving appropriate care[1]. Buprenorphine provides a more flexible outpatient treatment option compared to other medications. Additionally, its various prescription formulations enhance treatment accessibility, potentially leading to the development of dependence[2]. Therefore, the accurate determination of buprenorphine in human plasma samples is crucial for effectively monitoring treatment efficacy and adherence.

This study presents a sensitive and rapid extraction method using high performance liquid chromatography with UV detection for the determination of buprenorphine and its primary metabolite in commercial plasma. The sample volume of 0.5 mL was used in conjunction with MTBE (Methyl tert-butyl ether) as the extraction solvent. Optimization of extraction conditions for buprenorphine and its main metabolite from plasma was conducted to enhance extraction efficiency. Factors such as extraction volume, extraction time, and pH of the medium were systematically varied to achieve optimal conditions The optimized liquid-liquid extraction method achieved extraction efficiencies exceeding 90% for buprenorphine and its primary metabolite in plasma.

Hence, a novel HPLC-UV method was developed using a Kinetex F5 analytical column (150 mm × 4.6 mm i.d., 5 µm) with a mobile phase flow rate of 1 mL/min. The mobile phase consisted of ammonium acetate (20 mM), methanol, and acetonitrile; 55:20:25 (v/v/v). Detection was carried out at 210 nm, with a sample injection volume of 10 µL. The analysis time was 10 minutes, and both analytes were selectively analysed.

This rapid extraction and analysis method presents a promising approach for simultaneous detection of buprenorphine and its primary metabolite. The methodology provides a robust framework for monitoring treatment compliance and assessing therapeutic outcomes, which is crucial for individuals facing heightened risks of treatment failure.

References

[1] S. Jaeger Jr., B. Fuehrlein, Buprenorphine initiation to treat opioid use disorder in emergency rooms, J. Neurol. Sci. 411 (2020) 116716.
[2] M. Shulman, J.M. Wai, E.V. Nunes, Buprenorphine Treatment for Opioid Use Disorder: An Overview, CNS Drugs 33(6) (2019) 567-580.

Rapid Methods for Determining the Total Content of Jet Fuel in Soil for Forensic Environmental Studies

PSA-26

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Keywords: *Eco-friendly methods of analysis, Environment, GC-MS, Jet fuel, Petroleum*

The processes of extraction, transportation, storage and processing of oil and petroleum products very often become sources of environmental pollution, which can acquire catastrophic proportions.

Environmental pollution from oil and petroleum products (such as jet fuel, gasoline, diesel, lubricating oils, and fuel oil) is caused by increased hydrocarbon production and non-compliance with technical regulations during extraction, processing, and transportation. Oil hydrocarbons in the soil alter its physical and chemical properties and reduce the microbiota's functional activity. The production and processing of oil result in significant environmental pollution, accumulating hazardous oil waste and sludge, threatening human and wildlife habitat.

Soil contamination with petroleum hydrocarbons has been observed in all oil and gas fields of the Atyrau region, occurring at every stage of field development. This includes exploratory drilling, construction of production wells, operation, transportation, and storage of raw materials.

The need to monitor pollutants in the environment constantly drives advancements in environmental and analytical chemistry. Accurately determining very low concentrations of toxic chemicals in air, water, soil, and biological environments, and reliably detecting controlled components, demands high metrological standards for analytical methods. This includes accuracy, detection limits, selectivity, and precision.

Current methods for determining petroleum products in soil are labor-intensive, particularly during sample preparation. They involve extraction, purification from polar compounds, and concentration. These methods are not automated, take considerable time (15 to 380 minutes), and use toxic solvents like CCl_4, chloroform, and hexane. Solvent consumption ranges from 25 to 120 ml, and the need for evaporation or re-extraction (in IR spectrometry) results in significant emissions of toxic substances into the atmosphere.

In this regard, using gas chromatography-mass spectrometry (GC-MS) as a key analytical tool is the solution of the urgent task of quickly and accurately determining the contamination of the soil-geological environment with petroleum and jet fuel. It can allow to revolutionize the field of forensic ecology by improving effective analytical techniques.

By combining the sensitivity of mass spectrometry with the separation capability of gas chromatography, we aim to streamline the identification and quantitative analysis process, offering a valuable tool for forensic environmental studies. Implementing these developed GC-MS methods will significantly enhance the scientific and technical capabilities of environmental research organizations. Integrating advanced analytical tools will enable testing laboratories to work more efficiently, fostering innovation and boosting the competitiveness of research groups involved in pollution monitoring and remediation.

Results of performed lab research showed the effectiveness and eco-friendliness of used analytical tool. A 5 g soil sample was used. Optimal SPME conditions and equilibration times were established using a 100-μm PDMS fiber, ideal for extracting TPH from aqueous samples. The SPME parameters for extracting jet fuel from soil were pre-incubation time of 20 minutes, extraction time of 10 minutes, extraction temperature of 90°C, and desorption time of 5 minutes.

This study optimizes the method for quantitatively determining hydrocarbons in soil samples using headspace solid-phase microextraction (SPME) combined with gas chromatography-mass spectrometry (GC-MS). The effects of moisture content and solvent additives were examined. Results showed that increasing soil moisture content enhances hydrocarbon response, peaking at 15-20% depending on soil type and hydrocarbon concentration, before gradually decreasing.

The developed methods to be offered for use by the Institute of Forensic Examination, analytical laboratories for continuous analysis of oil and petroleum products in the soil. The creation of domestic methods makes it possible to commercialize services for the analysis of oil and petroleum products in the soil with inexpensive modern methods.

Due to the developed express methods of analysis and the introduction of advanced methods for analysis, the effectiveness of the state environmental control system will be significantly increased, which will have a beneficial effect on the health of the population.

Acknowledgements

Authors thank the Ministry of Science and Higher Education of the Republic of Kazakhstan for the grant funding for young scientists for scientific and (or) scientific and technical project No AP22789044.

A Survey of Total Selenium in Soil, Maize Plants, and Maize Flour by Inductively Coupled Plasma Tandem Mass Spectrometry (ICP-MS/MS): A Case Study for South Africa

PSA-28

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Keywords: *Inductively coupled plasma tandem mass spectrometry, Maize, Method validation, Selenium, Soil*

Selenium (Se) is a micronutrient that has multiple biochemical effects ranging from a nutritional deficiency at low levels to toxicity at high levels [1]. Its quantification in environmental systems is essential in improving the state of our knowledge and protecting the health of animals and people. The importance and status of selenium in South African mammals has been reviewed intensively in our previous publication [2]. South Africa is one of the countries reported to have low concentrations of Se in environmental samples, animals, and food products [3,4]. There is a need for scientific communities to continuously monitor and survey the status of Se micronutrients in the environment to support the governments in developing appropriate intervention strategies.

This study developed and validated methods to determine the total Se concentration in soil, maize plants, and maize flour. The methods were then utilized to survey the distribution of Se in three farming regions of South Africa.

Soil samples were collected at depths of 0-30 cm, followed by air-drying. Homogenization was achieved by crushing with an agate mortar and pestle to pass through a sieve (200 µm). Whole plant material was extracted from the corresponding soil, and separated into roots, leaves, and stems. Plant organs were dried in a drying oven and powders were attained by crushing using a Retsch GM 300 knife mill. Maize cobs from the corresponding plants were rinsed with tap water, followed by deionised water to remove any excess material. The cobs were dried in a drying oven, maize kernels were separated from the cob, and maize flour was obtained using a ZM 200 Retsch ultra-centrifugal mill.

All sample preparation was carried out gravimetrically, briefly 0.2-0.5 g aliquots were weighed into high-pressure Teflon vessels, and a suitable acid mixture was added, digestion was carried out utilising an Ethos UP microwave digestion system. Analysis was carried out using an Agilent 8900 Inductively coupled plasma tandem mass spectrometry (ICP-MS/MS), and interferences were removed using hydrogen as a reaction gas.

The performance of the methods was ascertained using matrix-certified reference materials (CRMs), namely NMIJ CRM 7303-a (trace elements in lake sediments), NIST SRM 1646-a (estuarine sediments), NIST SRM 1570-a (spinach leaves), NIST SRM 1571 (orchard leaves), NCS ZC 73010 (maize flour) and NIST RM 8437 (hard red spring wheat flour). All methods fulfilled the performance requirements of the AOAC International. An acceptable accuracy was achieved with percentage recoveries between 57 to 102% and $E_n - \mathrm{scores}$ within ±1 limits. Repeatability (RSD$_r$, %) and intermediate precision (RSD$_R$, %) ranged from 4 to 12%, and 9 to 15%, respectively. The limit of detection (LOD) and limit of quantification (LOQ) for soil were 0.024 ng g^{-1} and 0.082 ng g^{-1}, respectively. The LODs and LOQs for maize plants and flour were 0.0036 and 0.0179 ng g^{-1}, respectively. The performance characteristics of the methods were comparable with previously reported methods, confirming reliability. The measurement uncertainty was evaluated following the guide to the expression of uncertainty in measurement (GUM). Relative expanded uncertainty at a 95% level of confidence ($k = 2$) was less than 24% for the final measurement results for all the different matrices.

Total Se concentrations in soil were between 123 to 4349 ng g^{-1}, 2.5% of the tested samples were Se-deficient, 25% Se-marginal, 50% Se-sufficient, 20% Se-rich, and 2.5% Se-excessive. Selenium concentrations in maize plant organs were between 1 to 739 ng g^{-1}, The results also showed that the Se concentrations in maize plant organs did not meet the recommended Se concentration of 100 µg kg^{1} in animal feed to avoid Se deficiency in cattle. The Free State and Eastern Cape had Se deficient maize flour which did not meet the daily requirement of 40-400 µg day^{-1} from the World Health Organisation (WHO).

Acknowledgements

This work was supported by the National Metrology Institute of South Africa (NMISA), University of Johannesburg (UJ.), National Research Foundation (NRF) grant number **108508**, a University of Pretoria Paraclinical Science department, Department Agriculture & Rural Development (Tugela Ferry) and Villa Crop.

References

[1] A.A. Shaltout, J. Bouslimi, H. Besbes, the challenges of Se quantification in bean samples using line and continuum sources atomic absorption spectrometry, Food Chem. 328 (2020) 127124.

[2] N. Takata, J. Myburgh, A. Botha and P.N. Nomngongo, *The importance and status of the micronutrient selenium in South Africa: a review*, Environ. Geochem. Health (2021) 1–21.

[3] J.B.J. Van Ryssen, An evaluation of the trace element nutritional status of grazers in the eastern regions of the Free State and Mpumalanga, S. Afr. J. Anim. Sci. 7 (2006) 22–30.

[4] Z. Hattingh, C. Walsh, V. FJ, C. Bester, Micronutrient intake of HIV infected women in Mangauang, Free State, South African J. Clin. Nutr. 20 (2007) 28–36.

Quantitation of Intact Proteins in Biological Fluids Using CZE-MS with Off-Line Microelution SPE Sample Pretreatment

PSB-01

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Keywords: *Biological matrix, Capillary electrophoresis, Intact proteins, Preconcentration, Sample preparation*

Protein analysis in biological samples is one of the key areas of biomedical research. To miniaturize the entire analytical process and lower its environmental impact, attention is currently being paid to the development of new "greener" approaches and techniques aimed at the targeted determination of intact proteins, in contrast to the traditionally used approaches for protein analysis. In this field, capillary electrophoresis (CE) is becoming more popular and meets the criteria for greener techniques [1,2]. When combined with mass spectrometry (MS), it can compete with established chromatographic techniques in terms of performance and meets the requirements to become a routine part of practice [3,4]. However, when it comes to the analysis of biological matrices, its reliable application requires a comprehensive optimization of the separation and detection conditions in addition to the implementation of effective preconcentration techniques and pretreatment procedures [5].

In this work, we focused on the development of an on-line hyphenated capillary zone electrophoresis-mass spectrometry method (CZE-MS) employing off-line microelution solid-phase extraction (μSPE) based on hydrophilic-lipophilic balance (HLB) sorbent as a sample pretreatment step for the quantitation of multiple intact proteins with molecular masses <20 kDa in various biological fluids (human serum, plasma, urine, and saliva). Various preconcentration techniques can be used to enhance the sensitivity of the CZE-MS method [6,7]. 19- to 127-fold increase in signal intensity was achieved by employing transient isotachophoresis (tITP) as an in-capillary preconcentration method. Off-line μSPE with various eluate treatment procedures was evaluated to ensure the compatibility of the sample pretreatment method with the selected in-capillary preconcentration, separation, and detection process. Achieved extraction recoveries of spiked proteins were in the range of 76-100% for urine, 12-54% for serum, 21-106% for plasma, and 25-98% for saliva when the eluate was evaporated and reconstituted in the solution of the leading electrolyte to achieve the tITP process [8]. The optimum method was validated across different biological matrices, offering good linearity, accuracy, and precision, and making it suitable for proteomic studies (e.g., therapeutic drug monitoring, biomarker research) in different biological samples.

Acknowledgements

This work was supported by the projects VEGA 1/0483/20, VEGA 1/0514/22, and FaF/16/2024 and carried out in the Toxicological and Antidoping Center at the Faculty of Pharmacy Comenius University Bratislava. The project is based upon work from the Sample Preparation Study Group and Network supported by the Division of Analytical Chemistry of the European Chemical Society.

References

[1] P. M. Nowak, E. Sekuła, P. Kościelniak, White Analytical Chemistry: An approach to reconcile the principles of Green Analytical Chemistry and functionality, Chromatographia 83 (2020) 1133–1144.
[2] M. Ranasinghe, J. P. Quirino, Can we replace liquid chromatography with the greener capillary electrophoresis?, Curr. Opin. Green Sustain. Chem. 31 (2021) 100515.
[3] A. Stolz, K. Jooß, O. Höcker, J. Römer, J. Schlecht, C. Neusüß, Recent advances in capillary electrophoresis-mass spectrometry: Instrumentation, methodology and applications, Electrophoresis 40 (2019) 79–112.
[4] I. Mikšík, Coupling of CE-MS for protein and peptide analysis, J Sep Sci 42 (2019) 385–397.
[5] G. Jarvas, A. Guttman, N. Miękus, T. Bączek, S. Jeong, D. S. Chung, V. Pätoprstý, M. Masár, M. Hutta, V. Datinská, F. Foret, Practical sample pretreatment techniques coupled with capillary electrophoresis for real samples in complex matrices, Trends in Analytical Chemistry 122 (2020) 115702.
[6] T. Kawai, Recent Studies on Online Sample Preconcentration Methods in Capillary Electrophoresis Coupled with Mass Spectrometry, Chromatography 38 (2017) 1–8.
[7] L. Suntornsuk, O. Anurukvorakun, Sensitivity enhancement in capillary electrophoresis and their applications for analyses of pharmaceutical and related biochemical substances, Electrophoresis 43 (2022) 939–954.
[8] M. Opetová, R. Tomašovský, P. Mikuš, K. Maráková, Transient isotachophoresis–Capillary zone electrophoresis–Mass spectrometry method with off-line microscale solid phase extraction pretreatment for quantitation of intact low molecular mass proteins in various biological fluids, J. Chromatogr. A. 1718 (2024) 464697.

Targeted UPLC-ESI QQQ MS/MS Analysis of Bile Acids in Saliva and Gastric Juice: A Possibility for Early Non-Invasive Diagnosis of Barrett's Oesophagus

PSB-02

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Keywords: *Bile acids, LC-MS/MS, Saliva, SPE*

Bile acids (BAs) are a group of compounds essential for digestion and absorption of lipids with a steroid skeleton and a carboxylate side chain usually conjugated to glycine or taurine. BAs play a role as regulatory molecules for many metabolic processes and can be used as biomarkers for various illnesses [1].

In this project, we developed an accurate and sensitive method for the determination of BAs in saliva and gastric juice. Various aspects of sample collection and pretreatment by solid-phase extraction are discussed. Optimization of saliva sample collection included the following steps: comparison of two saliva collection methods (plain spitting and Salivette® saliva collection system), monitoring of BAs profile during the day, analysis of BAs stability in real samples, comparison of purification and concentration methods. Subsequently, reversed-phase ultra-performance liquid chromatography coupled with electrospray ionization triple quadrupole mass spectrometry operated in multiple reaction monitoring (MRM) mode was used for targeted detection and quantification of unconjugated BAs (UDCA, CDCA, DCA, HCA, CA, GLCA, LCA) and BAs conjugated to glycine (GUDCA, GCDCA, GDCA) or taurine (TUDCA, TCDCA, TDCA, TCA). The main parameters specific to each BA species are listed in **Table 1**. The major BAs in human saliva were GCDCA, GDCA, GUDCA, CA and CDCA. The limit of detection was determinated at 0.2-0.4 nmol/L.

Gastroesophageal reflux disease (GERD) is a common disease in which gastric contents enter esophagus. Reflux can damage the esophagus, pharynx or airways. GERD is often accompanied by symptoms such as heartburn or regurgitation. In some people, GERD can cause a change in the cells lining the lower esophagus, leading to Barrett's oesophagus. Barrett's oesophagus is associated with an increased risk of esophageal cancer [2].

Early detection and proper treatment of these patients are key factors in improving their prognosis. Therefore, the developed analytical approach was used in a study comparing the content of 15 BAs in saliva and gastric juice of healthy people and patients suffering from GERD or Barrett's oesophagus. BAs seem to be a promising marker for potential clinical use as an initial non-invasive diagnostic approach in such patients. Individual BA levels appear to be elevated in the saliva of patients with Barrett's esophagus compared to healthy volunteers. A larger clinical trial is currently going on.

Table 1. Main compound specific parameters of each BA species.

Bile acids	Abbreviation	Precursor ion	MRM	Retention time (min)
Taurochenodeoxycholic	TCDCA	$[M+HCOONa-H]^-$	498→80	1.2
Tauroursodeoxycholic	TUDCA	$[M+HCOONa-H]^-$		3.0
Taurodeoxycholic	TDCA	$[M+HCOONa-H]^-$		3.5
Glycoursodeoxycholic	GUDCA	$[M-H]^-$	448→74	1.4
Glycochenodeoxycholic	GCDCA	$[M-H]^-$		
Glycodeoxycholic	GDCA	$[M-H]^-$		
Taurocholic	TCA	$[M+HCOONa-H]^-$	514→80	1.9
Glycocholic	GCA	$[M-H]^-$	464→74	2.1
Ursodeoxycholic	UDCA	$[M+HCOO]^-$	437→391	2.6
Chenodeoxycholic	CDCA	$[M+HCOO]^-$		6.6
Deoxycholic	DCA	$[M+HCOO]^-$		6.9
Hyocholic	HCA	$[M+HCOO]^-$	453→407	2.8
Cholic	CA	$[M+HCOO]^-$		3.7
Glycolithocholic	GLCA	$[M-H]^-$	432→74	6.3
Lithocholic	LCA	$[M+HCOO]^-$	421→375	9.9

Acknowledgements

The authors acknowledge the financial support from the Ministry of Health of the Czech Republic (Grant no. NU23-00303) and the institutional support RVO: 68081715.

References

[1] V. Dosedelova, M. Lastovickova, J.F. Ayala-Cabrera, J. Dolina, S. Konecny, O.J. Schmitz, P. Kuban. Quantification and identification of bile acids in saliva by liquid chromatography-mass spectrometry: Possible non-invasive diagnostics of Barrett's esophagus? J. Chromatogr. A 1676 (2022) 463287.

[2] N.J. Shaheen, et al. Diagnosis and Management of Barrett's Esophagus: An Updated ACG Guideline. Am J Gastr. 117 (2022) 559-587.

One Step Derivatization and Switchable Hydrophilic Solvent Microextraction for the Determination of Adamantine Analogues in Human Urine by HPLC-FLD

PSB-03

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Keywords: *Amantamine analogues, Derivatization, Liquid chromatography, Microextraction, Switchable hydrophilicity solvent*

The present study describes an “one-step” derivatization and microextraction using a pH-switchable hydrophilicity solvent (SHS) for the determination of amantadine (AMA) and memantine (MEM) in human urine by HPLC and fluorescence detection. The procedure is based on the derivatization of the analytes with o-phthalaldehyde/N-acetyl cysteine at alkaline conditions (borate buffer pH 10.5) in the presence of sodium salicylate as extractant in a homogeneous solution. The liquid-solid transition of salicylic acid was achieved by adding an aliquot of concentrated H_3PO_4 due to the suppression of the carboxylic acid dissociation. The developed scheme enables efficient dispersion, phase separation and derivatization in a single step. The derivatives interact with the benzene ring of salicylic acid via hydrophobic interactions. Due to the moderate melting point of salicylic acid, its solidification is carried out at room temperature without the need for sample cooling. Critical parameters affecting the efficiency of the derivatization reaction and the microextraction performance were investigated and optimized. The analytes derivatives were monitored spectrofluorometrically ($\lambda_{ex}/\lambda_{em}$ = 340/450 nm). The proposed method was validated in terms of specificity, linearity, precision and accuracy. The method was linear in the range of 50 – 2000 ng mL^{-1} while the intraday and between days precision was less than 12% in all cases. The accuracy of the method ranged between 86-113%. The green character of the method was assessed. The applicability of the developed analytical scheme was demonstrated in authentic human urine samples.

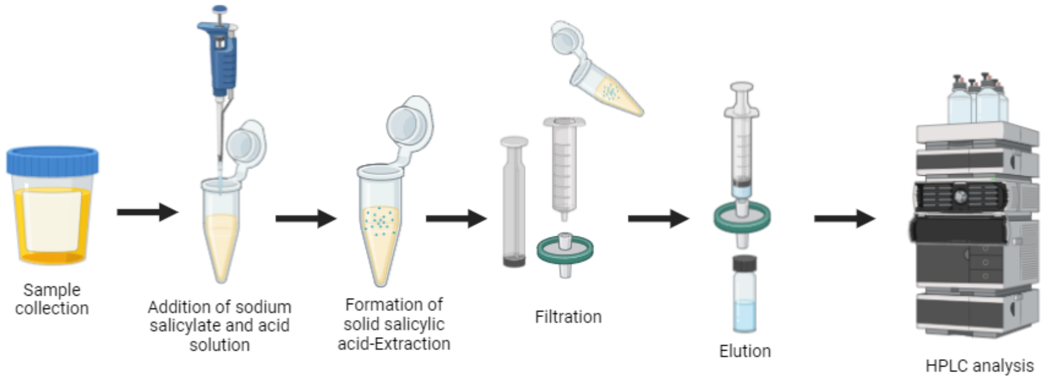

Figure 1. Graphical abstract of the microextraction protocol.

References

[1] N. Manousi, P.D. Tzanavaras, C.K. Zacharis, Microextraction based on liquid-solid phase transition of benzoic acid: Extraction of statins from human urine followed by chromatographic analysis, Talanta 266 (2024) 125088.
[2] Y. Basel, M. Rečlo, Y. Chubirka, Switchable hydrophylicity solvents in analytical chemistry. Five years of achievements, Microchemical Journal 157 (2020) 105115.

A Green Liquid Phase Microextraction Using Phthalic Acid as Switchable Hydrophilicity Solvent for the HPLC Determination of Sildenafil in Human Urine

PSB-04

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Keywords: *HPLC-UV, Liquid phase microextraction, Switchable-hydrophilicity solvent, Sildenafil, Urine*

Herein, a green liquid phase microextraction protocol using phthalic acid as switchable hydrophilicity solvent (SHS) is reported for the quantification of sildenafil in authentic human urine. The analyte was extracted onto phthalic acid solid particles which were produced through acidification of the sample. Its solidification was accomplished at ambient conditions without sample cooling. The determination of the sildenafil was carried out using high performance liquid chromatography-ultraviolet detection (HPLC-UV). The microextraction parameters that affect the extraction efficiency of the drug (i.e. SHS type and its concentration, acid type and concentration, extraction time, filter type) have been studied. The optimized analytical protocol involved the mixing of 300 μL of phthalate solution (0.75 M) with 600 μL of sample, followed by the addition of 50 μL of concentrated H_3PO_4. The produced solid was collected using membrane syringe filter (0.45 μm) and was finally dissolved in 500 μL of CH_3OH. Method validation data showed determination coefficient ≥ 0.99 for the linear range of 50 – 2000 ng/mL. The limit of detection (LOD) and the lower limit of quantitation (LLOQ) were 30 and 100 ng/mL, respectively. The accuracy (expressed as % recovery) of the method ranged between 88.0 – 108.9% while the precision (expressed as % RSD) was less than 17.8% in all cases. The robustness of the microextraction procedure and the instrumental method were investigated using Plackett-Burman experimental designs. The applicability of the method was demonstrated by analyzing authentic human urine samples after oral administration of drug-containing pharmaceutical formulation. The developed protocol offers cost-efficiency, handling simplicity, and high throughput. Its green character was evaluated using Green Analytical Procedure Index and Blue Applicability Grade Index.

References

[1] M. Terzi, M. Theodorou, E. Louloudi, N. Manousi, P.D. Tzanavaras, C.K. Zacharis, Salicylic acid as a switchable hydrophilicity solvent for the microextraction of the antibiotic amphotericin B from human urine followed by HPLC-UV analysis, Microchemical Journal 199 (2024) 110025.
[2] Y. Basel, M. Rečlo, Y. Chubirka, Switchable hydrophylicity solvents in analytical chemistry. Five years of achievements, Microchemical Journal 157 (2020) 105115.

Dispersive Pipette Tips Extraction for Vitamin K Analysis

PSB-05

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Keywords: *Microextraction, Pipette tips, Vitamin K*

Despite advancements in analytical techniques, sample preparation remains a critical step for analyzing certain compounds in biological materials. Several trends are currently emerging, focusing on improving the robustness and reproducibility of methods, removing matrix compounds, enhancing analyte recovery, and analyte preconcentration. Additionally, sample miniaturization and sustainability are gaining prominence, integrating green chemistry principles to reduce the environmental impact of methods.

One innovative microextraction technique is dispersive pipette extraction (DPX), a miniaturization of the conventional solid-phase extraction (SPE) method. DPX tips incorporate an SPE sorbent material loosely contained within the tip, allowing dynamic mixing with the sample solution. This approach enables efficient extraction of analytes using low volumes of sample and organic solvents, reduces extraction time and sample manipulation, achieves high recovery, exhibits high efficiency, and allows the possibility of automation, making it a valuable tool for various analytical applications [1,2].

Commercial DPX pipette tips have been tested as a miniaturized sample preparation tool for determining vitamin K in human serum. The determination of vitamin K is challenging in many aspects. Preconcentration of the sample and its purification are essential since vitamin K, unlike other fat-soluble vitamins, is present in human serum at very low concentrations, typically only in units of nmol/L. It is also crucial to consider the light sensitivity of vitamin K and its limited solubility, which can result in its adhesion to various surfaces, further complicating the analysis.

To select the best device, the commercial microextraction pipette tips with various sorbents were compared according to their extraction efficiency. The liquid-liquid extraction was used as the reference method with 100% recovery [3]. Based on the physicochemical properties of the analyte and sample composition, six different types of DPX tips were tested: XTR tips with Supel™ Swift HLB (10 mg) (copolymer with hydrophilic and lipophilic balance properties), C18 (30 mg), C18 (10 mg), WAX-S (5 mg +20 mg salt), WAX-S (5 mg + 40 mg salt) (weak anion exchange (WAX) sorbent with a secondary amine phase with a styrene-divinylbenzene backbone in combination with salt (S)), and Supelco HybridSPE® (30 mg) (zirconia coated silica). Multiple sample preparation protocols for six pipette tip microextractions were employed, including those recommended by manufacturers and those developed in-house and adapted from published ones for the conventional SPE format. Two distinct workflow approaches were used. For XTR tips with Supel™ Swift HLB and tips with C18 sorbent, a three-step bind-wash-elute process was utilized, in which the target analyte is first bound to the sorbent, then interfering substances are removed by washing, and finally, the analyte is eluted from the sorbent. A clean-up workflow was applied when using WAX-S and Supelco HybridSPE® tips. WAX-S pipette tips contain WAX sorbent for clean-up and the salt required for supported liquid-liquid extraction (SALLE). This combination of DPX and SALLE is particularly suitable for procedures involving the extraction of hydrophobic analytes, where acetonitrile is used as a precipitating agent. Sample purification is achieved even when using pipette tips containing zirconia coated silica, which selectively removes phospholipids from biological samples [4].

In addition to evaluating the extraction efficiency using different DPX tips, other factors were considered, including sample volume, use of organic solvents, and procedure difficulty. The results obtained by this study and a comparison of the methods will be presented.

Acknowledgements

The study was supported by Charles University (GA UK No. 121124) and by the University Hospital in Hradec Králové MH CZ DRO (UHHK, 00179906). Authors also acknowledge the Ministry of Health projects NU21J-02-00021 and NW24-05-00031. All rights reserved.

References

[1] Ch. Suwanvecho, L. Kujovská Krčmová, F. Švec, Effective, convenient, and green sample preparation for the determination of retinol and retinol acetate in human serum using pipette tip microextraction, Talanta. 262 (2023) 124689.

[2] D. C. M. Bordin, M. N. R. Alves, E. G. de Campos, B. S. De Martinis, Disposable pipette tips extraction: Fundamentals, applications and state of the art, J. Sep. Sci. 39 (2016) 1168-1172.

[3] K. Mrštná, K. Matoušová, L. Kujovská Krčmová, A. Carazo, J. Pourová, P. Mladěnka, L. Matysová, F. Švec, Analysis of vitamin K1 and major K2 variants in rat/human serum and lipoprotein fractions by a rapid, simple, and sensitive UHPLC-MS/MS method, J. Chromatogr. A. 1714 (2024) 464548.

[4] DPX Technologies. https://dpxtechnologies.com/xtr/

Blood Microsampling Devices in Global Untargeted Metabolic Profiling

PSB-06

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Keywords: *Microsampling, Sample Preparation, Untargeted metabolomics*

Untargeted metabolomics is an analysis strategy that aims to obtain an overall profile of the molecules in a biological sample, and can be used in large-scale studies for biomarker identification. Considering the constraints to perform said studies, such analysis could largely benefit from microsampling strategies. Microsampling devices allow for the easy collection of very small volumes of blood, however, different devices might yield distinct results. The aim of the present work was to evaluate the difference in the untargeted blood profiles obtained with different microsampling devices, namely Dried Blood Spots, Volumetric Absorptive Microsampling (Mitra) and Capitainer cards.

To achieve this goal, a whole blood untargeted analysis method was developed, using an UHPLC with a Reverse Phase system, coupled to a TIMS-TOF working in DDA mode. MS conditions were optimized to increase sensitivity and reduce in-source fragmentation, to obtain the most detailed chromatographic profile possible, while facilitating trustful annotations. Extraction protocols were optimized based on literature surveys [2,3]. Among the different solvents tested (acetonitrile, methanol and water, both individually and at different proportions), acetonitrile:methanol mixture in a ratio of 70:30 yielded the most favorable outcomes, considering number features, area of annotated peaks and reproducibility. Data processing and analysis was performed by different software (i.e. MSDial, XCMS, Metaboscape)

Afterwords, each individual device underwent a similar optimization process. Methanol: H2O demonstrated to be the most efficient solvent. To increase sensitivity and improve chromatographic profile, samples underwent evaporation and reconstitution in a reduced volume of water-methanol mixture at a ratio of 95:5. Finally, we compared the untargeted profiles obtained from ten individuals using the three different microsampling devices and plasma samples, under the optimized analysis conditions.

Acknowledgements
Funded by the European Union "Harmonising and Unifying Blood Metabolomic Analysis Networks" BLOOD METABOLOMIC ANALYSIS NETWORKS" (Project number: 101073062) which is implemented under the Action " Horizon Europe - MARIE SKLODOWSKA-CURIE ACTIONS (Doctoral Networks)". Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them.
Biomic_AUTh, Center of Excellence in Metabolomics research (BiACEM)" (Project number: 101079370), which is implemented under the Action "Horizon Europe Twinning grant.

References

[1] D.M.S. Silva, M. Thaitumu, G. Theodoridis, H. Witting, Gika, Volumetric Absorptive Microsampling in the Analysis of Endogenous Metabolites. Metabolites 13 (2023) 1038.

[2] A.D. Southam, L.D. Haglington, L. Najdekr, A. Jankevics, R.J.M. Weber, W.B. Dunn, Assessment of human plasma and urine sample preparation for reproducible and high-throughput UHPLC-MS clinical metabolic phenotyping, Analyst. 145 (2020) 6511-6523.

[3] W.B. Dunn, D. Broadhurst, P. Begley, et al., Procedures for large-scale metabolic profiling of serum and plasma using gas chromatography and liquid chromatography coupled to mass spectrometry, Nat Protoc. 6(7) (2011) 1060-1083.

Dried Blood Spot Devices: Precise, Convenient, and Patient-Friendly Devices for Analysis of Vitamin A and E

PSB-07

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Keywords: *Commercial DBS, Microsampling technique, Vitamin A, Vitamin E*

Recent advancement in analytical instrumentation and methodologies have enabled the use of low sample volumes for analysis, leading to the development of microsampling techniques. Dried blood spots (DBS) are commonly used in clinical research and practice to minimize the invasiveness of blood sampling. This approach involves using a lancet to collect small quantities of whole blood from the fingertip, which is then applied to filter paper card for drying. DBS eliminates the need for venipuncture and pre-storage sample preparation, making it an ideal blood sampling method for challenging populations such as neonates and elderly patients, as well as people stayed in remote areas. Additionally, DBS sample can be shipped as non-hazardous material due to the reduced biohazard risk of dried blood. Compared to conventional DBS card, like Whatman 903 protein saver card, the newer commercial options with volumetric microfluidic chip minimize analytical bias though accurate blood volume sampling and reduced the hematocrit effects [1]. These devices also enhance the convenience of home sampling for patients.

This study compares the extraction efficiency of 2 commercial DBS devices, Hemaxis and Capitainer B, along with the conventional Whatman 903 protein saver card, based on their recoveries. Vitamin A and E are well-known for their essential antioxidant properties and significant immunomodulatory effects. Vitamin A acts as a cofactor in T-cell proliferation and differentiation, while vitamin E influences T cell function by affecting T-cell membrane Integrity, signal transduction, and cell division. Moreover, low levels of vitamin A and E have been reported in hospitalized SAR-CoV-2 infected patients [2-4]. Therefore, these vitamins are our analytes of interest. Our developed whole blood extraction method served as reference method, with its recovery set at 100%. Factors influencing extraction efficiency such as wetting and extracting solvents, extracting methods and duration, were optimized to achieve satisfactory and repeatable result. Chromatographic condition for determination of vitamin A and E was adopted from our previous study [5]. Despite the advantages of these commercial DBS devices over the conventional ones, there are some challenges related to the design of devices and extraction procedures. For Hemaxis, the need to close the protective cover after each blood collection for transferring sample to filter card is inconvenience for self-sampling, and the device's four-spot capacity may be excessive. In the other hand, there are more chances to collect the samples if incomplete spots are created. For Capitainer B, the volumetric microfluidic chip is challenging to fill due to its perpendicular location to the collecting site, requiring a larger blood drop. Conversely, the micro-channel position of Hemaxis is more flexible, easier to contact and adsorb the blood drop via capillary force. For extraction, the lipophilic nature of vitamin A and E necessitates the use of non-polar solvents as additives in the wetting solvent.

This method has the potential for use in the future pandemics and local disease outbrakes where patient mobility is restricted. Furthermore, this blood sampling technique can support the telemedicine, allowing patients to avoid hospital visits while enabling healthcare providers to obtain results and offer advice though modern telecommunication methods.

Acknowledgements

The study was supported by project SVV 260 662, UHHK the University Hospital in Hradec Králové MH CZ DRO (UHHK, 00179906), NU22-01-00151 and NU21J-02-00021. All rights reserved.

References

[1] J.D. Freeman, L.M. Rosman, J.D. Ratcliff, P.T. Strickland, D.R. Graham, E.K. Silbergeld., State of the Science in Dried Blood Spots, Clin. Chem. 64(4) (2018) 656-679.

[2] L. Kujovská Krčmová, L. Javorská, K. Matoušová, P. Šmahel, M. Skála, M. Kopecký, C. Suwanvecho, N. Přívratská, D. Turoňová, B. Melichar, Evaluation of inflammatory biomarkers and vitamins in hospitalized patients with SARS-CoV-2 infection and post-COVID syndrome, Clin. Chem. Lab. Med. 62(6) (2024) 1217-1227.

[3] A. Carazo, K. Macáková, K. Matoušová, L. Kujovská Krčmová, M. Protti, P. Mladěnka, Vitamin A Update: Forms, Sources, Kinetics, Detection, Function, Deficiency, Therapeutic Use and Toxicity, Nutrients. 13(5) (2021) 1703.

[4] E.D. Lewis, S.N. Meydani, D. Wu, Regulatory role of vitamin E in the immune system and inflammation, IUBMB Life. 71(4) (2019) 487-494.

[5] L. Urbánek, D. Solichová, B. Melichar, J. Dvořák, I. Svobodová, P. Solich, Optimization and validation of a high performance liquid chromatography method for the simultaneous determination of vitamins A and E in human serum using monolithic column and diode-array detection, Anal. Chim. Acta. 573-574 (2006) 267-272.

Modernizing Diagnostics: Efficient Routine Vitamin K Analysis with a Focus on Metabolic Disorders

PSB-08

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Keywords: *Extraction, Menaquinone, Phylloquinone, Sample preparation, Vitamin K*

Vitamin K, in its forms of phylloquinone (vitamin K1) and menaquinones (varieties of vitamin K2), differs in its activity and affects blood clotting, bone metabolism, and other biological processes. Vitamin K is the least well understood of the four fat-soluble vitamins, and a knowledge of its levels can provide crucial information about its role in the human body and potential impact on metabolic disorders. However, analysis of these vitamins is challenging. They are present in the blood in nanomolar concentrations, so it is important to ensure proper sample preparation and sensitive detection. Mass spectrometry has become a method of choice in the detection of these analytes, but is obscured with a high matrix effect. In addition, light sensitivity, high lipophilicity, protein binding, or tendency to adhesion of container wall complicates the preparation of the sample. LLE or SPE were usually used for this purpose. Unfortunately, these techniques are laborious and are not very feasible for clinical laboratories and vitamin K is not commonly analyzed [1–3].

The aim of our work was to achieve the most effective extraction technique for vitamin K, specifically its forms K1 and menaquinones MK 4, MK 7, and MK 9 in serum, which would be suitable for use in an everyday clinical laboratory. The target was to avoid laborious, time-consuming, multistep sample preparation which uses large sample and organic solvent volumes, or increase the sensitivity of the method by enlarging the sample injection volume. We compared traditional sample preparation approaches with modern methods such as supported liquid extraction, micro-LLE, or Phree™ phospholipid removal plate. We tended to miniaturization in a term of sample or consumed solvent volumes leading to patient-friendlier, environmentally-friendlier, cheaper, and faster methods. The impact was placed on its application for large series of samples using exclusively tools available on the market [3]. Later on, the main objective was to analyze the phylloquinone and menaquinones in patients who suffer from metabolic disorders. The serum samples from the entire cohort of 150 patients who are treated as outpatients at the University Hospital Hradec Králové were evaluated and results discussing the correlation between levels of vitamin K and diabetes of type I and II or dyslipidemia will be presented.

Acknowledgements

This study was supported by Charles University by project SVV 260 662, by the University Hospital in Hradec Králové MH CZ DRO (UHHK, 00179906), funded by the Ministry of Health of the Czech Republic via grants NU21J-02-00021 and NW24-05-00031. All rights reserved.

References

[1] P. Mladěnka, K. Macáková, L. Kujovská Krčmová, L. Javorská, K. Mrštná, A. Carazo, M. Protti, F. Remião, L. Nováková, the OEMONOM researchers and collaborators, Vitamin K – sources, physiological role, kinetics, deficiency, detection, therapeutic use, and toxicity, Nutr. Rev. 80 (2022) 677–698.

[2] K. Mrštná, K. Matoušová, L.K. Krčmová, A. Carazo, J. Pourová, P. Mladěnka, L. Matysová, F. Švec, Analysis of vitamin K1 and major K2 variants in rat/human serum and lipoprotein fractions by a rapid, simple, and sensitive UHPLC-MS/MS method, J. Chromatogr. A 1714 (2024) 464548.

[3] K. Mrštná, D. Turoňová, C. Suwanvecho, F. Švec, L.K. Krčmová, The power of modern extraction techniques: A breakthrough in vitamin K extraction from human serum, Microchem. J. 198 (2024) 110170.

Analysis of Biothiols in Non-Invasive Samples by Capillary Electrophoresis with Laser Induced Fluorescence and Amine Group Derivatization

PSB-09

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Keywords: *Biothiol, Capillary electrophoresis, Nanoparticles, Preconcentration*

Biothiols are analytes of emerging importance, as their altered levels in different bodily fluids may signalize different pathological states, such as cardiovascular disease or Alzheimer’s Disease, to name a few. [1] While methods for the analysis of biothiols in blood samples were already developed, their determination in non-invasive samples, such as saliva or exhaled breath condensate (EBC), is still under research. [2] In this work, a novel strategy for biothiol preconcentration on gold nanoparticles is combined with the derivatization of the amino group and capillary electrophoresis with laser induced fluorescence-detector (CE-LIF) is used for separation and sensitive detection.

Since the concentrations of biothiols (e.g. cysteine, homocysteine, or glutathione) in non-invasive samples, such as EBC, are extremely low, large volume of sample is collected. This is achieved by a lab-made device with cascade collection tube design, which allows collection of several mililiters of EBC in reasonable time. The collected EBC sample is treated with gold nanoparticles and the biothiols from the sample are selectively adsorbed on the gold surface. After the supernatant containing sample matric, but free of adsorbed analytes is removed, the biothiols are desorbed by the addition of dithiothreitol, 2-mercaptoethanol or thioglycolic acid. Finally, a derivatization step is performed prior to the CE-LIF analysis.

Usually, derivatization is performed with a reagent, that is reactive towards the sulfhydryl group of the biothiol. This approach works in case when only the analytes are present in the sample. However, when excessive concentrations of other thiol-containing molecules are present in the sample, this may hamper the analyte derivatization and subsequent separation. In the case of gold nanoparticle concentration approach, the analytes are desorbed from the Au surface using dithiothreitol, 2-mercaproethanol, or similar thiol-containing compound. This results in the excess of desorbing reagent present in the sample and the abovementioned problems.

To solve this problem, we developed a new approach in which the derivatization is performed via the amine group, rather than thiol group of the biothiols. A new LIF detector for capillary electrophoresis was constructed to suit this reaction mechanism. To minimize interferences, the thiol group of the biothiols was blocked by the addition of *N*-ethylmaleimide first. Then, different derivatization reagents (fluorescamine, naphthalene-2,3-dicarboxaldehyde, or AlexaFluor NHS ester) and separation conditions were tested and optimized. Using this approach, biothiols can be analyzed in samples with large extent of other thiol-group containing compounds in nanomolar to micromolar concentrations.

Acknowledgements
The authors acknowledge financial support from Czech Science Foundation (grant 22-23815S) and the institutional support RVO:68081715.

References

[1] M. Isokawa, T. Kanamori, T. Funatsu, M. Tsunoda, Analytical methods involving separation techniques for determination of low-molecular-weight biothiols in human plasma and blood, J. Chromatogr. B 964 (2014) 103–115.
[2] V. Dosedělová, P. Kubáň, Investigation of interactions between biological thiols and gold nanoparticles by capillary electrophoresis with laser-induced fluorescence, Electrophoresis (2024) 1-10.

Investigation of Biologically Active Components from Karatau Eryngium (Eryngium Karatavicum Iljin)

PSB-10

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Keywords: *Antifungal, Biopesticides, Eryngium karatavicum Iljin, GC/MS, Plant extracts*

Eryngium Karatavicum Iljin, also *known as Karatau Eryngium*, is a thorny herb from the Apiaceae family that grows in stony pastures and meadows in the Karatau Mountains in southern Kazakhstan. This plant has been found to contain bioactive compounds such as flavonoids, essential oils, and fatty acids that have potential antifungal properties. However, research on the full composition of Eryngium and its potential use as a natural alternative to synthetic biopesticides for controlling grape diseases is still lacking.

The aim of this study is to investigate the component composition of Eryngium Karatavicum Iljin. For this purpose, the following objectives were set:

- To determine the optimal extraction methods (maceration, hot extraction, subcritical fluid extraction CO_2, ultrasonic bath).
- To study the constituent composition of the extracts obtained by GC/MS and to evaluate their potential for the overall antifungal efficacy of the extract.

Before extraction, the plant material was cleaned of extraneous impurities, dried to remove excess moisture at room temperature (20-25 °C) to avoid thermal degradation of the components, and ground to obtain a homogeneous sample with particle size up to 1 - 5 mm.

The optimal extraction methods for each plant material were determined as follows:

- Maceration (using 96% ethanol for 10 days with ultrasonication for 1 hour) allowed the extraction of 36 plant compounds, including 15% terpenoids, 16% esters, and 4% fatty acids, among others.
- Hot extraction (at 78-80 °C for 8 hours) isolated 60 plant compounds, with 6% being terpenoids, 11% esters, 14% fatty acids, and other compounds.
- An ultrasonic bath (at 35-40 °C for 8 hours) extracted 60 compounds, with 12% being terpenoids, 21% esters, 35% fatty acids, and others.
- Subcritical fluid extraction CO_2 (57-65 kg/m^2, 18-23 °C, 8 hours) allowed the isolation of 37 compounds, of which 50% are terpenoids, 19% are esters, and 11% are fatty acids. Comparing this extraction method with other extraction methods, subcritical fluid extraction CO_2 has been identified as a promising method for extracting the target compounds from Eryngium Karatavicum Iljin, which has antifungal properties. This is due to the simplicity and cost-effectiveness of the method. The chemical analysis of the Eryngium extract revealed the presence of the falcarinol (1.71%) compound, which has antifungal activity, as well as several other compounds such as caryophyllene, (0.39%), beta-bisabolene (0.6%), manool (1.78%), corymbolone (6.52%), γ-Tocopherol (0.4%), vitamin E (2%), phytol acetate (5%), phytol (31%) and friedelanol (18%). The chemical and biological study of the properties of plant extracts, the search for new types of biologically active substances, and the development of biopesticides from the raw materials of the endemic species *Eryngium Karatavicum Iljin* are all important aspects in the development of the agricultural industry. Based on an analysis of the literature, it has been noted that there is a need to develop such biopesticides using raw materials from endemic plant species in Kazakhstan.

Acknowledgements
This research is funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP19680563).

Geographical Origin Authentication of Cretan Thyme Honey Using Vacuum-Assisted Headspace Solid-Phase Microextraction

PSB-11

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Keywords: *Geographical origin**,** Headspace solid phase microextraction, Honey, Vacuum, Volatiles*

Honey is renowned worldwide for its nutritional, health, and medicinal benefits [3]. Its unique aroma arises from a complex mixture of volatile compounds, which vary depending on the floral origin of the nectar collected by bees [1]. To prevent mislabeling and ensure the authenticity of honey products, the European Union mandates the inclusion of both botanical and geographical origins on honey labels [1]. Traditionally, pollen analysis has been employed to verify the floral origin of honey, but this method is labor-intensive and requires specialized knowledge. [1,3]. As an alternative, Headspace Solid-Phase Microextraction (HS-SPME) has become widely adopted for differentiating and classifying honeys based on their volatile profiles [1,2]. This solvent-free, simple, and sensitive technique is effective, although it is limited by the time required for analytes to reach equilibrium among the sample, gas phase, and extractant phase [5].

This study aimed to distinguish the geographical origin of Cretan thyme honey based on its volatile profile using Vacuum-assisted Headspace Solid Phase Microextraction Arrow (Vac-HS-SPME Arrow). The use of vacuum conditions was expected to enhance the extraction kinetics of analytes with low headspace affinity [5], while the Arrow configuration addressed limitations of traditional SPME devices, such as mechanical robustness and limited extraction phase volume [4]. Extraction parameters, including time and temperature, were optimized under both vacuum and atmospheric pressure conditions, and the performance of Vac-HS-SPME was compared with that of conventional HS-SPME. The results demonstrated that Vac-HS-SPME outperformed regular HS-SPME, detecting more compounds and achieving higher overall extraction efficiency across various time and temperature combinations. The optimal conditions for Vac-HS-SPME were determined to be an extraction temperature of 60°C with a sampling time of 15 minutes, significantly shorter than the 60 minutes required for HS-SPME. The optimized Vac-HS-SPME approach was then applied to the geographical determination of 40 Greek thyme honey samples. Principal Component Analysis (PCA) successfully discriminated Cretan thyme honey from samples originating from the North Aegean, Cyclades, Dodecanese, Peloponnese, and Thessaly regions based on their volatile content.

Acknowledgements
This work was funded by the Hellenic Foundation for Research and Innovation (HFRI).

References

[1] L.F. Cuevas-glory, J.A. Pino, L.S. Santiago, A review of volatile analytical methods for determining the botanical origin of honey, Food Chem. 103 (2007) 1032–1043.
[2] I.K. Karabagias, A. V. Badeka, S. Kontakos, S. Karabournioti, M.G. Kontominas, Botanical discrimination of Greek unifloral honeys with physico-chemical and chemometric analyses, Food Chem. 165 (2014) 181–190.
[3] X. Zhang, H. Gu, R. Liu, X. Qing, J. Nie, A comprehensive review of the current trends and recent advancements on the authenticity of honey, Food Chem. 19 (2023) 100850.
[4] S. Pellacani, C. Durante, S. Celli, M. Mariani, A. Marchetti, M. Cocchi, L. Strani, Optimization of an analytical method based on SPME-Arrow and chemometrics for the characterization of the aroma profile of commercial bread, Chemom. Intell. Lab. Syst. 241 (2023) 104940.
[5] E. Psillakis, The effect of vacuum: an emerging experimental parameter to consider during headspace microextraction sampling, Anal. Bioanal. Chem. 412 (2020) 5989-5997.

Enhancing Oxidative Stability Analysis in Adult Nutrition Formulas Using Microextraction Techniques and GC-MS

PSB-12

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Keywords: *Adult formula, Carbonyl compounds, DLLME, SPME, VOC*

Medical nutrition formulas provide complete or supplemental nutrition for adults unable to meet their dietary needs through regular food intake [1]. Used in various clinical situations, they meet specific dietary requirements, including macronutrient and micronutrient proportions, and are tailored for needs like glucose control, immune support, or increased protein [1]. Ensuring food safety is crucial for these consumers with other health issues and compromised immune systems. Carbonyl compounds and volatile organic compounds (VOCs) in these formulas result from lipid and protein oxidation, accelerated by factors like high processing temperatures, light exposure, and metal ions [2,3]. These compounds pose risks such as toxicity, adverse health effects, reduced flavor and odor, gastrointestinal discomfort, inflammation, and decreased nutrient intake [2]. Long-term effects may include chronic inflammation and metabolic disorders from oxidative byproducts accumulation [2-4]. Currently, no specific analytical methods exist for detecting carbonyl compounds and VOCs in adult formulas, leading to inaccurate estimations of potentially toxic compounds like α-dicarbonyls, malondialdehyde, and acrolein [1,2].
Here, targeted and untargeted GC-MS analysis of adult formulas is presented to first profile VOCs and identify potentially toxic organic compounds using HS-SPME [3], and also quantitatively determine six carbonyl and dicarbonyl compounds, including malondialdehyde, formaldehyde, acetaldehyde, acrolein, methylglyoxal, and diacetyl, by DLLME with DNHP derivatization.

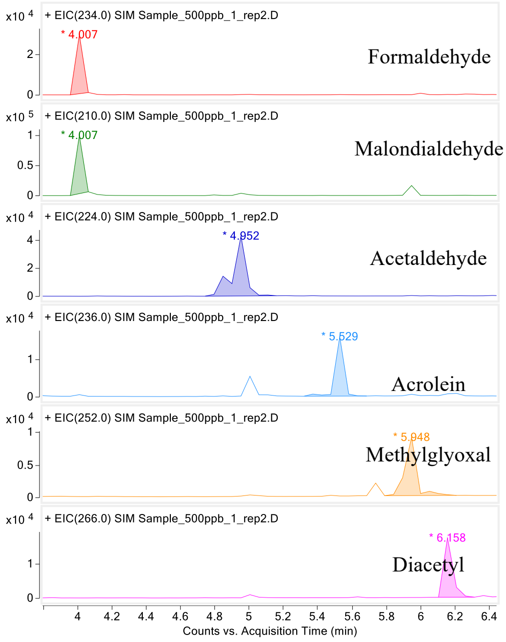

Figure 1. GC-Ms chromatogram of carbonyl compounds at 500 µg/g in adult formula.

DLLME was adapted from a previous study [4] through a comprehensive matrix extension study according to the FDA analytical method validation, achieving great results in terms of linearity (r2>0.9992), intraday and interday precision (%RSD < 10.2%), and accuracy (%recovery between 91.2-104.3). HS-SPME revealed variations in VOCs of two adult formulas stored at different temperatures for one month compared to freshly opened formulas. DLLME was used for the targeted analysis of carbonyl compound variations during this time in five adult formulas, and for the occurrence study of 13 adult formulas. Statistical analyses, including principal component analysis (PCA), hierarchical clustering analysis (HCA), and the plotting of heatmaps, revealed correlations between the decrease in volatile compounds present in the samples and storage time and temperature. This study provides valuable insights into the stability of carbonyl compounds and VOCs in adult formulas under various storage conditions, contributing to the understanding of food quality and safety.

Acknowledgements

The research is supported by the Polish National Science Center within withing the project 2023/07/X/NZ9/01113 as part of the MINIATURA-7 program and the Spanish Ministry of Science, Innovation, and Universities (Project RTI2018-096450-B-100) and FEDER fund.

References

[1] M. Hellerman Itzhaki, P. Singer, Advances in medical nutrition therapy: parenteral nutrition, Nutrients, 12(3) (2020) 717.
[2] J.A. Custodio-Mendoza, A.M. Ares-Fuentes, A.M. Carro, Innovative Solutions for Food Analysis: Microextraction Techniques in Lipid Peroxidation Product Detection, Separations 10 (2023) 531.
[3] H.J. Clarke, D.T. Mannion, M.G. O'Sullivan, J.P. Kerry, K.N. Kilcawley, Development of a headspace solid-phase microextraction gas chromatography mass spectrometry method for the quantification of volatiles associated with lipid oxidation in whole milk powder using response surface methodology, Food chemistry 292 (2019) 75-80.
[4] J.A. Custodio-Mendoza, C. Caamaño-Fernandez, A. Lage, P.J. Almeida, R.A. Lorenzo, A.M. Carro, GC–MS determination of malondialdehyde, acrolein, and 4-hydroxy-2-nonenal by ultrasound-assisted dispersive liquid-liquid microextraction in beverages, Food Chemistry 384 (2022) 132530.

Bisphenols Content in Mussel as Sentinel of Surface Sea Waters Coming from Galician Rías

PSB-13

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Keywords: *Bisphenols, Mussel, Water quality, Galician Rías*

Bisphenols (BPs) are widely used in manufacture of different products as paints, adhesives and plastics. They are present in food packing, personal care products (PCPs), metal cans, toys and medical devices. They are added to plastics during production to improve their properties for industrial and domestic applications. As BPs are weakly bound to the polymer matrix, are susceptible to migration from plastics to marine environment such as water and bivalve mollusc. BPA and its analogues were found in wastewater, rivers, ground water, surface water, marine water and sediment, and biota samples in high concentrations [1].

Mussels have been considered as sentinels (Mussel Watch Programme) of marine environmental to evaluate the coastal status and temporal trends identifying the potential sources of pollution. The aim of this work is to give the levels of nine bisphenols (BPAF, BPF, BPE, BPA, BPG, BPC2, BPZ, BPS and BPM) in wild and raft mussel (*Mitylus galloprovincialis*) used as bioindicator of water quality and collected during 2022 in the Rías de Eo, Foz, Viveiro, Barqueiro, Ortigueira, Celeiro, Ferrol, Ares-Betanzos, A Coruña, Costa da Morte, Corme-Laxe, Camariñas, Corcubión, Muros-Noia, Arousa, Pontevedra and Vigo (wild mussel) and in the Rías de Ares-Betanzos, Muros-Noia, Arousa, Pontevedra and Vigo (raft mussel).

Analyses of mussel were carried out in pools of 30 individuals. Lyophilized samples were extracted using the miniaturized MSPD (Matrix Solid Phase Dispersion) with C_{18} sorbent. The extracts were purified by using Captiva EMR-lipid and then derivatized using BSTFA + 1% TMCS. Finally, the cold extracts were analysed by GC-MS (Agilent 6890-Agilent MS 5973N, Wilmington, DE, USA) in SIM Mode.

Levels of SBPs ranged from 20 ng/g dry weight to 23584 ng/g dry weight. The BPA was the majority compound, followed by BPF and BPS that are industrial substitutive of BPA. As it usually happens with anthropic pollutants, wild mussels presented the highest levels of SBPs, they live near the coast partially submerged in the sea water. There was a clear difference between the content of bisphenols in mussels coming from Rías Altas and Rías Baixas. Mussels from Rías Altas had the highest levels of SBPs. The Rías Altas, highly populated and industrialized, were constituted by Rías de Eo, Foz, Viveiro, Barqueiro, Ortigueira, Celeiro, Ferrol, Ares-Betanzos, A Coruña, Costa da Morte, Corme-Laxe, Camariñas, Corcubión, and the Rías Baixas, wider and deeper than Rías Altas, are constituted by Rías de Muros-Noia, Arousa, Pontevedra and Vigo.

Acknowledgements
This research was funded by the Spanish *Agencia Estatal de Investigación* MCIN/AEI/10.13039/501100011033 through the project PID2020-117686RB-C32 and FEDER/ERDF funds and co-financed by the European Regional Development Fund through the Interreg VI-A Spain-Portugal Programme (POCTEP) 2021-2027, Project 0048_BLUE_WWATER_1_E).

References
[1] N. Salgueiro-Gonzalez, I. Turnes-Carou, L. Viñas, V. Besada, S. Muniategui-Lorenzo, P. López-Mahía, D. Prada-Rodriguez, Mar. Pollut. Bull. 106(1-2) (2016) 360-365.

Fast HPLC-UV for Total Amino Acid Determination through Ultrasound-Accelerated Acid Hydrolysis

PSB-14

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Keywords: *Amino acid, Acid hydrolysis, Fmoc-Cl, Plant protein, Ultrasound*

In recent years, there has been an increasing demand for efficient methods to analyze amino acids in various applications, particularly in the food and pharmaceutical industries. Amino acids are fundamental building blocks of proteins and play crucial roles in nutrition, flavor, and product quality. Accurate and rapid determination of total amino acids is essential for ensuring product quality, nutritional labeling compliance, and meeting regulatory requirements [1].

Traditional methods for amino acid analysis often involve lengthy hydrolysis processes and the use of hazardous chemicals, posing challenges in terms of time, safety, and environmental impact [2]. Moreover, with the growing emphasis on sustainability and green chemistry practices, there is a need to develop analytical methods that minimize resource consumption, waste generation, and environmental harm [3].

Here, a universal and groundbreaking approach for rapid Total Amino Acid Determination utilizing Ultrasound-Accelerated Acid Hydrolysis coupled with Fast HPLC-UV analysis is presented. This novel method significantly reduces hydrolysis time from 24 hours to just 1 hour, marking a substantial advancement in efficiency. Following hydrolysis, free amino acids derived from vegetable proteins undergo rapid derivatization with Fmoc-Cl solution within a mere 10 minutes at room temperature, facilitating expedited analysis by HPLC-UV within 15 min employing a Kinetex C18 2.6 µm (50 x 2.1 mm) column with core shell technology.

Notably, we explore the incorporation of ethanol and citric acid as greener alternatives to conventional mobile phase compositions. Through an extensive parameter optimization process employing an asymmetrical screening design, various factors including sample size, pH, acid type, derivative reagent concentration, and derivatization time are evaluated to enhance method effectiveness.

The optimized method demonstrates exceptional linearity ($R^2 < 0.999$), accuracy (between 180-120 % recovery), and precision (%RSD < 15%). Validation studies confirm the method's suitability for determining total amino acids in diverse plant-based proteins such as soy, rice, and insect proteins. This innovative approach holds significant promise for accelerating amino acid analysis while promoting environmentally friendly practices in analytical chemistry.

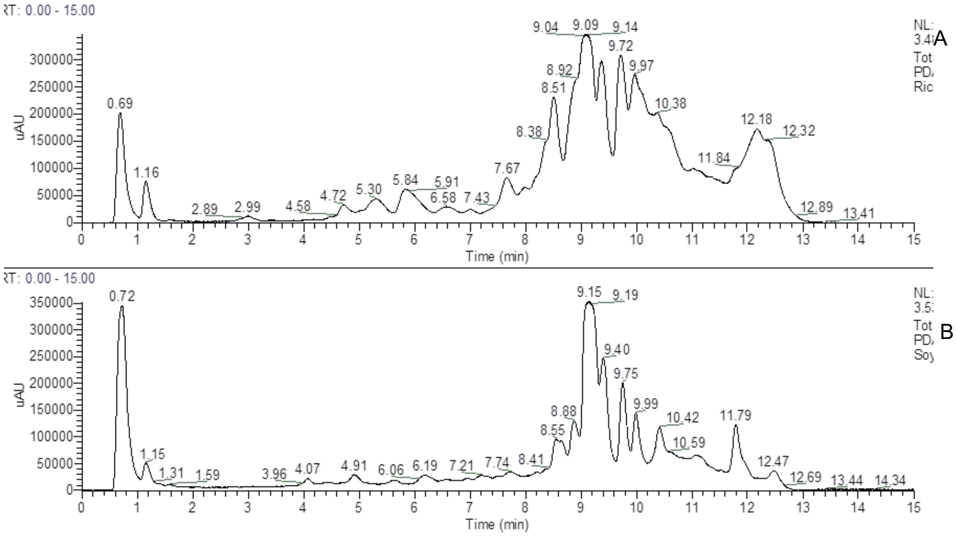

Figure 1. HLPC-UV chromatogram of total amino acids determination in rice (A) and soy (B) protein isolates.

Acknowledgements
The research is covered within the project “Coacervation of double emulsions with anthocyanins using plant-based proteins" funded by the SONATA program of the Polish National Science Center - project no: 2021/43/D/NZ9/01572.

References

[1] Rebane, R., & Herodes, K. Comparison of three buffer solutions for amino acid derivatization and following analysis by liquid chromatography electrospray mass spectrometry. J. Chrom. A 1245 (2012) 134-142.9.
[2] Łozowicka, B., Kaczyński, P., & Iwaniuk, P. Analysis of 22 free amino acids in honey from Eastern Europe and Central Asia using LC-MS/MS technique without derivatization step. J. Food Comp. Anal. 98 (2021) 103837.
[3] Sajid, M., & Płotka-Wasylka, J. Green analytical chemistry metrics: A review. Talanta, 238 (2022) 123046.

Comparison of Microwave-Assisted Saponification and Extraction Methods for MOH Determination in Meat

PSB-15

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Keywords: *LC-GC-FID, LC-GCxGC-FID, Meat, Mineral oil hydrocarbons, Microwave-assisted saponification*

Mineral oil hydrocarbons (MOH) are a complex mixture of liposoluble environmental and processing contaminants of petrogenic origin. They may pose different toxicological risks to humans depending on their structure (i.e., saturated (MOSH) or aromatic (MOAH)) [1]. The increasing interest in more detailed information on the composition of MOH is driving a shift from LC-GC-FID, considered the routine technique, to more advanced techniques, notably LC-GCxGC-FID. Moreover, due to the complexity of MOH and food matrices, an efficient sample preparation method must be performed. One of the steps commonly included in the sample preparation for MOH analysis is saponification, which allows the complete extraction of MOH from the lipids present in the matrix [2]. Nonetheless, this step impacts the distributions of some internal standards used for quantification due to a different partition in the solvent phases [3]. This study aimed to compare two different microwave-assisted saponification and extraction (MASE) methods for the analysis of MOH in various types of meat.

Three different types of unprocessed meat (raw bacon, pig rib, and beef rib) were chosen. The samples undergo two different MASE procedures: i) KOH saturated solution in methanol (MASE 1) followed by a washing step with 40 mL of water plus 3 mL of methanol, and the vessels were kept at −18 °C for 30 min before recovering the hexane phase [4]; or ii) a KOH 2 M in EtOH/H_2O (1/1 v/v) (MASE 2), followed by the addition of 20 mL of H_2O and storing the vessels 20 min in the fridge before recovering the hexane phase. The methods were evaluated in terms of internal standards distribution and recovery. The results confirmed that the partition of the standards tri-tert-butyl benzene (TBB) and 2-methyl naphthalene (2-MN), which are commonly used to quantify MOAH, depended on the MASE method applied. The differences in recovery between both standards were higher when MASE 1 was applied, showing a lower recovery of 2-MN compared to TBB (ratio TBB/2-MN of 1.24 on average). When MASE 2 was applied, the ratio TBB/2-MN (ratio of 1.06 on average) was closer to their expected proportion in the internal standard (ratio of 1), which guarantee a better representativeness of the MOAH extraction and prevent differences between the results when quantifying with TBB or 2-MN. The ratio between the two standards was consistent among the different meat types tested.The accuracy of both MASE methods for MOSH was higher than 90% in both spiked levels (added levels of ≈1.6 and 3.6 mg/kg). For MOAH (added at the same levels as MOSH), the accuracy was lower when MASE 1 was applied (73 – 80%) in comparison to MASE 2 (95 – 97%).

Acknowledgement
The authors thank Milestone, LECO and Restek for their support.

References

[1] EFSA, Update of the risk assessment of mineral oil hydrocarbons in food, J. EFSA 21 (2023) 1–143.
[2] S. Bratinova., et al., Guidance on sampling, analysis and data reporting for the monitoring of mineral oil hydrocarbons in food and food contact materials, 2nd ed., Publications Office of the European Union, Luxembourg, 2023.
[3] G. Bauwens, G. Purcaro, Improved microwave-assisted saponification to reduce the variability of MOAH determination in edible oils, Anal. Chim. Acta 1312 (2024) 34278.
[4] P. Albendea, C. Conchione, L. Menegoz Ursol, S. Moret. A study on mineral oil hydrocarbons (MOH) contamination in pig diets and its transfer to back fat and loin tissues, Animals 14 (2024) 1450.

Aptamer-Modified Magnetic Nanoparticles for Extraction of Milk Protein Allergen α-Lactalbumin from Foodstuffs

PSB-16

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Keywords: *α-Lactalbumin, Allergenic protein, Aptamer, Magnetic solid-phase extraction, Selective Sorbent*

Food allergies have garnered significant interest due to the high prevalence of immune sensitization to certain food components across the population. The Food and Agriculture Organization has identified eight global priority food allergen categories, which include milk and milk products. Specifically, cow's milk and dairy products are the primary cause of food allergies in infants, with the protein α-lactalbumin (α -LA) being one of the most significant allergenic proteins. Therefore, in order to ensure consumers' safety, it is essential to develop accurate and sensitive methods for detecting and quantifying allergenic proteins in foods. In this regard, magnetic solid-phase extraction (MSPE) has proven to be a highly efficient, simple, low-cost, and environmentally friendly strategy for extracting target compounds from complex matrices. In addition, it is possible to use different affinity ligands in order to increase MSPE selectivity. Among these ligands, aptamers (Apts) have emerged as innovative and stable recognition molecules, being particularly notable for their ability to isolate biomacromolecules such as proteins.

In this work, Apt-modified magnetic nanoparticles were used as MSPE sorbent for the selective isolation of the milk protein allergen α-LA from different foodstuffs. For this purpose, a thiol-terminated aptamer was immobilized onto the surface of vinylized MNPs via "thiol-ene" click chemistry reaction. The resulting Apt-modified VMNPs were characterized and several parameters (such as loading and elution solvents, extraction and desorption temperature and time, loading capacity and breakthrough volume) that affect the Apt-MSPE efficiency were investigated. Under the optimal conditions, the developed Apt-based MSPE protocol was applied to different foodstuffs susceptible of containing non-declared milk traces.

Acknowledgements

The authors acknowledge financial support from the Spanish State Research Agency (AEI//10.13039/501100011033/), the Spanish Ministry of Science, Innovation and Universities (MICIU) and the European Union (NextGenerationEU/PRTR) through project PID2021-125459OB-I00. Also, the authors acknowledge the projects CIGE/2023/069, CIAICO/2022/183 and INVEST/2022/107 funded by Generalitat Valenciana. The authors extend their appreciation to MICINN for granting the Spanish Network of Excellence in Sample preparation (RED2022-134079-T). This communication is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society.

Design and Application of a 3D-Printed Device Coated with Solid-Phase Extraction Resins: An Alternative to QuEChERS for Extraction and Quantification of Five Pesticide Residues in Honey Samples via UHPLC-UV

PSB-17

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Keywords: *Honey, Pesticides, QuEChERS, 3D-printed device, UHPLC-UV*

The QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe) method is the current preferred approach for pesticide residue extraction in food matrices due to its robust and efficient sample preparation capabilities [1,2]. However, recent advancements have explored the use of stereolithographic 3D-printed devices coated with solid-phase extraction (SPE) resins, demonstrating promising recoveries in extracting xenobiotics from environmental samples [3]. This study aimed to develop a straightforward 3D-printed device coated with five different SPE cartridges—C18 (Sigma Aldrich, St Louis, MO, USA), BakerbondTM SPE (Avantor, Gliwice, Poland), Oasis HLB and Oasis MCX (Waters, Milford, MA, USA), and Strata X (Phenomenex, Torrance, California, USA)—and to evaluate its performance.

These devices were assessed for their efficiency in extracting five pesticides—azoxystrobin, carbaryl, pirimicarb, thiacloprid, and thiamethoxam—previously reported to be present in honey samples. Following extraction, the pesticides were eluted with suitable solvents and quantified using a new, simple, and robust UHPLC-UV method in gradient mode. The separation was completed in less than 15 minutes using a Kinetex 5 μm Biphenyl, 100 Å, 50 × 2.1 mm column, with a mobile phase composed of methanol and 0.1% formic acid at pH 3.65, achieving effective separation for all five pesticides.

The method demonstrated good linearity up to 100 μM, with R^2 values higher than 0.995 for all pesticides, detection limits as low as 3.25 μM, and good interday precision with RSD values lower than 10%. The analysis of real honey samples confirmed the presence of the studied pesticides, demonstrating the practical applicability of the validated methodologies for routine monitoring of honey. The recoveries for Strata X and Oasis MCX cartridges were higher than 80%, outperforming the QuEChERS method, which had average recoveries exceeding 70%. Additionally, the devices exhibited reusability properties, enhancing their practical utility. This novel approach provides an effective alternative to QuEChERS for pesticide residue analysis in honey, offering improved reliability, sensitivity, and efficiency.

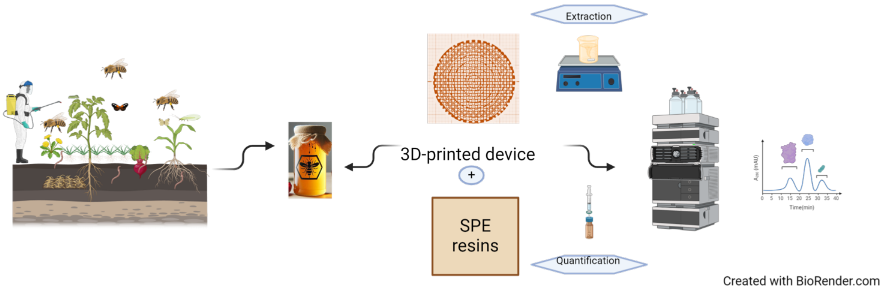

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Figure 1. Honey pesticide contamination and analytical approach.

Acknowledgements
Financial support from the University of Medicine, Pharmacy, Science and Technology "George Emil Palade" of Târgu Mures, internal grant contract number 164/18/10.01.2023.

References

[1] V. Tripathy, S. Devi, G. Singh, R. Yadav, K. Sharma, R. Gupta, K. Tandekar, A. Verma, S. Kalra, Development and Validation of Tandem Mass Spectrometry-Based Method for the Analysis of More than 400 Pesticides in Honey. J. Food Compos. Anal.128 (2024) 106013.

[2] Y. Makni, T. Diallo, F. Areskoug, T. Guérin, J. Parinet, Optimisation and Implementation of QuEChERS-Based Sample Preparation for Identification and Semi-Quantification of 694 Targeted Contaminants in Honey, Jam, Jelly, and Syrup by UHPLC-Q/ToF High-Resolution Mass Spectrometry. Food Chem. 425 (2023) 136448.

[3] D. Barzallo, E. Palacio, J. March, L. Ferrer, 3D Printed Device Coated with Solid-Phase Extraction Resin for the on-Site Extraction of Seven Sulfonamides from Environmental Water Samples Preceding HPLC-DAD Analysis, Microchem J. 190 (2023) 108609.

Development of a Direct Liquid-Liquid Extraction Method Combined with UHPLC-DAD for the Determination of Seven Flavonoids in Extra Virgin Olive Oil

PSB-18

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Keywords: *Extra virgin olive oils (EVOOS)**,** Flavonoids, Ultra-high-performance liquid chromatography with diode array detection (UHPLC-DAD), Liquid-liquid extraction (LLE)*

Extra virgin olive oil (EVOO) is an unrefined olive oil, that allows retraining the full flavor profile and nutritional properties of olive oil. Flavonoids are a secondary metabolism that occurs naturally in the plant kingdom. Their strong antioxidant behavior led to preventing and protecting from a wide kind of diseases. Flavonoids are the main antioxidants existing in EVOO. Their type and concentration differ as the kind of olive and the planting, geographical, storage and olive pressing conditions. EVOO's profiling flavonoids are crucial in the determination of EVOO quality

In this work, a direct LLE technique has been developed for fast extraction of seven main flavonoids (rutin, luteolin, isorhoifolin, taxifolin, kaempferol, apigenin and isorhamnetin) from EVOO samples. In this context, 10 mL of EVOO sample was directly extracted by 0.5mL of methanol due to 15 min of sonication preventing a long lipid washing and dilution steps. Regarding the polarity of the dissolvent of flavonoids (methanol), that is not mixed with oil, sample spik is not normally achievable. Solving this problem, sample enrichment technique was performed by mixing the flavonoids standard mixture solution with the oil for 1h directly before under nitrogen evaporation of methanol residual [1,2]. The spiked sample is used for the optimization of sample preparation, recovery, and the enrichment factor study.

However, a novel UHPLC-DAD analytical approach has been developed and optimized for the identification and quantification of flavonoid compounds in EVOOs. For this purpose, high efficiency C_{18} column was used with the combination with ACN and acidified water (pH=3.6) as a mobile phase in a gradient mode. The successful separation was done in total of 28 minutes. The proposed method allows for the simultaneous determination of the mentioned seven flavonoids, with good resolution between peak pairs and high sensitivity, LOD $\leq$0.05 ug mL^{-1} with %RSD $\leq$2.5%.

The development of direct LLE method, reduce the consumption of solvents (up to 79% comparing with previous work) [3] and the total extraction time (up to 50%) that traditionally employed for the cleaning up the oily samples from the lipide content and oil phase dilution before the extraction process, addition to the solvent evaporation and residue redissolve. Besides, the developed UHPLC-DAD method is the first for the determination of seven flavonoids in EVOO samples. Allowing to profile the olive oil flavonoids content that led to EVOO enhancement classification as well as quality improvement of commercial EVOOs.

References

[1] L. Pizarro, M. Becerra, A. Sayago, M. Beltran, R. Beltran, Comparison of Different Extraction Methods to Determine Phenolic Compounds in Virgin Olive Oil, Food Analytical Methods 6 (2013) 123-132.

[2] D. Bongiorno, V. Di Stefano, S. Indelicato, G. Avellone, L. Ceraulo. Bio-phenols determination in olive oils: Recent mass spectrometry approaches, Mass Spec Rev. 42 (2023)1462-1502.

[3] M. Becerra, A. Vélez, A. Ramos, P. Ritcher, R. Beltran, A. Sayago. Characterization and evaluation of phenolic profiles and color as potential discriminating features among Spanish extra virgin olive oils with protected designation of origin, Food Chemistry 241 (2018) 328-337.

Improving Juice Processing Quality and Efficiency with a Novel Pectin Lyase

PSB-19

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Keywords: *Clarification, Fruit juice processing, GC-FID, Liquefaction, Pectin lyase*

Microbial pectinolytic enzymes are widely used in a variety of industrial sectors, most notably the fruit juice industry, for the clarification, liquefaction, and stabilization of juices [1]. These enzymes breakdown the pectins in fruit pulp by cleaving α-1,4 glycosidic linkages between galacturonosyl residues. Pectin lyase is the only known pectinase that can degrade highly esterified pectins, found in different fruits, into short molecules by the β-elimination reaction. The use of pectin lyases for the degradation of pectin is advantageous over other pectin-degrading enzymes because no methanol is produced during processing [2].

Our research focused on the unique pectin lyase, produced by *Bacillus velezensis* 16B, with the aim of improving fruit juice processing. Pectin lyase was successfully expressed in *E. coli* and purified by metal affinity chromatography. The recombinant enzyme exhibited robust activity under alkaline conditions and excellent thermal stability. Treatment of apple and orange juices with recombinant enzyme significantly increased juice yield and clarity without generating excessive methanol, as confirmed by GC-FID, making it a promising candidate for fruit juice processing. One of the common issues with juice processing is its acidity, which prevents the addition of external nutrients and decreases storage stability. Neutralization of naturally acidic juices, such as apple and orange juices, gives way for the creation of stable bases into which additional nutrients, such as proteins, can be incorporated. Recombinant *B. velezensis* pectin lyase has an activity optimum under neutral to slightly basic pH conditions, thus making it ideal for the processing of neutralized juices and the production of great bases for different beverages.

Acknowledgements

This research was supported by the University of Belgrade - Institute of Chemistry, Technology and Metallurgy through the "Seed Research Grant" for young scientists ("Fruit Juice Quality Improvement with Tailored Enzyme Mix - FruitEnMix"), financed by Serbia Accelerating Innovation and Entrepreneurship Project (SAIGE).

This research was supported by the Ministry of Science, Technological Development and Innovation of Republic of Serbia (Contract numbers: 451-03-66/2024-03/200026 and 451-03-65/2024-03/200168).

References

[1] M. Pavlović, A. Margetić, A. Leonardi, I. Križaj, M. Kojić, Z. Vujčić, M. Šokarda Slavić, Improvement of fruit juice quality: novel endo-polygalacturonase II from Aspergillus tubingensis FAT 43 for enhanced liquefaction, clarification, and antioxidant potential, Food Funct. **15(6)** (2024) 2906 – 2919.

[2] N. Sharma, M. Rathore, M. Sharma, Microbial pectinase: sources, characterization and applications. Rev. Environ. Sci. Biotechnol. 12 (2013) 45–60.

Extraction and Determination of Steroid Saponins in Tribulus Terrestris Nutraceuticals with Validated UHPLC-CAD Method

PSB-20

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Keywords: *Charged-Aerosol detector, Nutraceuticals, Phenyl-Hexyl column, Steroid saponins, Tribulus terrestris*

The presented work describes the development, extraction and validation of a new UHPLC method for simultaneous determination of steroidal saponins in nutraceuticals supporting sexual potency based on Tribulus terrestris extracts. Following saponins were analysed: dioscin, diosgenin, protodioscin, pseudoprotodioscin, gitogenin, gracillin, tribulosin, sarsasapogenin, and ruscogenin. The method was subsequently used for the analysis of these substances in food supplements that were available on the Czech market - Afroditky Plus (FYTOPHARMA), ALIVER Tribulus (ALIVER nutraceuticals spol. s.r.o.), Menactive (ADVANCE nutraceuticals, s.r.o.), ALAVIS Maxima Bestier (Patron ca, s.r.o.), Allnature Kotvičník (Allnature, s.r.o.), Dr. Popov Kotvičník (Dr. Popov, s.r.o.), ADIEL Kotvičník zemní (Ing. Stanislav Kameníček), Clavin (Simply You Pharmaceuticals), Arginmax (Simply You Pharmaceuticals), 3BULLUS (Dr.Max), Primulus (Primulus Group), and Tribul (ADVANCE). The separation was performed on the Kinetex® Phenyl-Hexyl (100 × 4.6 mm; 2.6 μm) chromatography column at the temperature of 15°C, using gradient elution program with mobile phase consisting of acetonitrile and 0.1% formic acid solution at flow rate of 1.0 ml min^{-1}. The analytes were detected by Charged-aerosol detector (CAD), which was more suitable than conventional Diode-Array Detector due to the lack of chromophore in many of the analyzed compounds.

The samples were prepared by extracting food supplements with the mixture of acetonitrile, ethanol, and ultrapure water (2:6:3, v/v/v), sonicated 10 minutes and filtrated through 0.22 μl PTFE filter. Subsequently, the content of active substances in the commercially available nutraceuticals was evaluated and the quality of individual producers was compared.

Acknowledgements
The authors would like to thank to Czech Science Foundation through the project no. 23-05586S, and Charles University project no. SVV 260 662.

Plant-Based and Same Great taste? Finding Off-Flavours Causing Negative Consumer Perception of Pea Milk Using High Capacity Sorptive Extraction (HiSorb)

PSB-21

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Keywords: *Environmental, GC-MS, Malodours, Odourants, Plant-based*

In recent years, the use of plant-based milk products has grown considerably across the globe, with European sales growing by 21% between 2020 and 2022 to reach a record €5.8 billion in revenue. This has been due to rising popularity of vegan, vegetarian and flexitarian diets compared with more traditional animal based dairy diets, as well as consumers becoming more climate and health conscious. The rise in popularity is also attributed to consistent improvement and alignment of the alternative products to the taste of the 'original' products. A comprehensive profile of the plant-based food is key for showing both the desirable flavour compounds, and highlighting the undesired off-odour within the plant-based product. Particularly with alternative milk products, reoccurring off-odours have been highlighted as bean-like and grassy notes, which studies have shown that low-level pyrazine compounds could be a possible reason [1,2].

Headspace extraction is typically the sampling strategy of choice to replicate the odour sensation which consumers experience when interacting with the food product, but it is limited in its sensitivity and is strongly affected by water ingress. By using a sorptive extraction technique coupled with a backflushed focusing trap, odorants can be pre-concentrated and water can be easily removed prior to analysis. Sorptive extraction can not only extract analytes from the headspace, but by immersion of the probes too. The combination of using multiple phases and immersive sampling is explored in this study to extract a fuller aroma profile of the alternative milk without heating the sample.

High capacity sorptive extraction (HiSorb) was used to encapsulate a wide volatility/polarity range with use of the three phase probe Divinylbenzene (DVB) /carbon wide range (CWR)/polydimethylsiloxane (PDMS).Several previously unknown flavour active compounds were extracted (e.g. benzyl cis-cinnamate providing spicy-floral notes and 4-anisaldehyde giving a sweet, floral odour). These compounds were not detected when sampling the headspace via SPME-trap. As pea milk has a high-water content, the trap purging step enabled removal of unavoidably sampled water while analytes of interest remained unaffected. This also led to improved chromatography and increased column and detector lifetime. Here we show a wide range of analytes were extracted including the targeted pyrazines, demonstrating that a comprehensive flavour profile can be established.

References

[1] C.Zhang, Y. Hua, X. Li, X. Kong, Y. Chen, Key volatile off-flavor compounds in peas (Pisum sativum L.) and their relations with the endogenous precursors and enzymes using soybean (Glycine max) as a reference, Food. Chem. 333 (2020) 127469.

[2] Y. Liu, C. Cadwallader, M.A. Drake, Identification of predominant aroma components of dried pea protein concentrates and isolates, Food Chem. 406 (2023) 134998.

Enzymatic Production and HPLC-RID Analysis of Prebiotic Oligosaccharides in Functional Foods

PSB-22

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Keywords: *Enzymes, Food analysis, HPLC-RID, Oligosaccharides, Prebiotics*

In recent years, there has been a growing demand for functional oligosaccharides (OS), predominantly in the form of prebiotics and soluble fibers [1]. These OS are synthesized through chemical or enzymatic means, although enzymatic methods are considered more suitable and preferable due to the favorable impact on the environment and bioeconomy. Fructooligosaccharides (FOS), as well-established prebiotics, are corroborated by their well-documented benefits [2]. They exhibit antioxidant activity, amplifying their allure as functional food additives in animal feed, food and beverages where they serve as partial fat and sugar substitutes, bulking agents, or companions to high-intensity artificial sweeteners, ameliorating post-consumption taste perceptions [1,3]. Xylooligosaccharides (XOS), not only demonstrate prebiotic efficacy, but have also demonstrated anti-inflammatory, antiallergic and antioxidant properties [4]. The development of rapid and sensitive analytical techniques for the quantification of OS in food, along with the optimization of process and biological analysis, is a fundamental part of the development of functional food products [5].

Therefore, we standardized and validated the most suitable and affordable tailored HPLC-RID method, with high resolution and sensitivity for the routine analysis of two major groups of prebiotics, FOS and XOS, following the recommendations of the ICH (the International Council on Harmonization). The method usability was tested in complex samples obtained by in-house produced fungal enzymes. The analyzed OS were prepared by fungal enzyme extracts, with or without prior purification of individual enzymes, from naturally isolated carbohydrates (xylan and inulin). The validation showed highly satisfactory parameters – high precision, accuracy, sensitivity, working range, and specificity. The method is applicable on the same column with the same mobile phase, for more than one type of OS of different origin. It has been successfully employed for precise and unambiguous detection of both types of OS in complex mixtures (rich in interfering compounds), rendering it a promising candidate for the detection of other oligosaccharide samples, including enzymatically treated juices.

In this study, it was shown that this method is also applicable for examining and quantifying the presence of XOS and FOS in food and beverage samples, including various types of milk (such as cow's milk, almond milk, rice milk, soy milk, and coconut milk), yogurt, and juices (such as apple juice) where these oligosaccharides have been detected. Such a method would be useful for laboratories engaged in researching various types of oligosaccharides, which is a common practice when studying new prebiotics and developing new methods for their characterization and quantification. It is also valuable for food analysis and quality control.

Acknowledgements

This research was supported by the University of Belgrade - Institute of Chemistry, Technology and Metallurgy through the "Seed Research Grant" for young scientists ("Fruit Juice Quality Improvement with Tailored Enzyme Mix - FruitEnMix"), financed by Serbia Accelerating Innovation and Entrepreneurship Project (SAIGE).
This research was supported by the Ministry of Science, Technological Development and Innovation of Republic of Serbia (Contract numbers: 451-03-66/2024-03/200026 and 451-03-65/2024-03/200168).

References

[1] O.O. Ibrahim, Functional Oligosaccharide: Chemicals Structure, Manufacturing, Health Benefits, Applications and Regulations, J. Food. Chem. Nanotechnol. 4 (2018) 65-76.
[2] G.R. Gibson, R. Hutkins, M.E. Sanders, S.L. Prescott, R.A. Reimer, S.J. Salminen, K. Scott, C. Stanton, K.S. Swanson, P.D. Cani, K. Verbeke, G. Reid, Expert consensus document: The International Scientific Association for Probiotics and Prebiotics (ISAPP) consensus statement on the definition and scope of prebiotics, Nat. Rev. Gastroenterol. Hepatol. 14 (2017) 491–502.
[3] C.G. Kumar, S. Sripada, Y. Poornachandra, Status and Future Prospects of Fructooligosaccharides as Nutraceuticals, in: Role of Materials Science in Food Bioengineering. Elsevier, 2018, pp. 451–503.
[4] C. de Freitas, E. Carmona, M. Brienzo, Xylooligosaccharides production process from lignocellulosic biomass and bioactive effects, Bioact. Carbohydr. Diet. Fibre. 18 (2019) 100184.
[5] K.F. Catenza, K.K. Donkor, Recent approaches for the quantitative analysis of functional oligosaccharides used in the food industry: A review. Food. Chem. 355 (2021) 129416.

Rapid Analysis of Phenolic Compounds in Plant-Based Milk Alternatives: A Smartphone-Based Approach

PSB-23

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Keywords: *Colorimetry, Matrix isolation, Plant-based milk alternatives, Smartphone, Total phenol content*

The popularity of plant-based or non-dairy milk alternatives is increasing as a dietary preference [1]. Phenolic compounds, essential constituents of these alternatives, contribute to their health benefits as abundant antioxidants. However, conventional methods for determining total phenolic content are often time-consuming and involve complex procedures especially in the presence of complex matrix analysis [2]. This study aims to develop a novel and miniaturized method for determining phenolic compounds in plant-based milk using digital image colorimetry on smartphones as a fast and cost-effective analysis method, along with the possibility of in-situ analysis. The procedure involves the application of the classically used Folin-Ciocalteu reagent for performing a color-forming reaction, followed by the extraction of derivative into the in-situ generated supramolecular solvent (Fig.1). The formation of such a solvent is observed due to the application of the green surfactant alkyl polyglycoside C_8-C_{10} as an amphiphile and heptanoic acid as coacervation agent. The micellar solution facilitates efficient extraction, overcoming challenges posed by matrix components such as ash, protein, carbohydrate, crude fibre, and other interfering substances contents [3]. Digital images were captured inside a box under controlled lighting conditions and analyzed with image processing algorithms. Various types of plant-based milk substitutes, including plant extracts of cereals, legumes, nuts, seeds, and pseudocereals, have been analyzed. The results obtained, compared with reference methods, demonstrate significant findings, with a slope of the Passing-Bablok equal to 1.0024, indicating results are in good agreement. Moreover, assessments of the greenness based on the AGREE tool show a total score of 0.85, meaning that the procedure is environmentally friendly with a low environmental footprint [4].

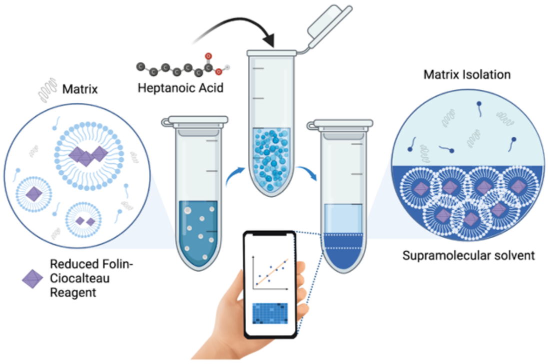

Figure 1. Rapid analysis of total phenolic content using smartphone.

References

[1] F. Reyes-Jurado, N. Soto-Reyes, M. Dávila-Rodríguez, A.C. Lorenzo-Leal, M.T. Jiménez-Munguía, E. Mani-López, A. López-Malo, Plant-Based Milk Alternatives: Types, Processes, Benefits, and Characteristics, Food Reviews International 39:4 (2023) 2320-2351.
[2] Aydar, E. F., Mertdinç, Z., Demircan, E., KocaÇetinkaya, S., &Özçelik, B., Kidney bean (Phaseolus vulgaris L.) milk substitute as a novel plant-based drink: Fatty acid profile, antioxidant activity, in-vitro phenolic bio-accessibility and sensory characteristics. Innovative Food Science & Emerging Technologies 83 (2023) 103254.
[3] C. Vakh, S. Koronkiewicz, Surfactants application in sample preparation techniques: Insights, trends, and perspectives. TrAC Trends in Analytical Chemistry 165 (2023) 117143.
[4] F. Pena-Pereira, W. Wojnowski, M. Tobiszewski, AGREE—Analytical GREEnness Metric Approach and Software. Analytical Chemistry 92(14) (2020) 10076–10082.

Influence of Grape Pomace Addition on the Nutritional and Functional Value of Maize Extrudates

PSB-24

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Keywords: *Antioxidant capacity, Grape pomace, Maize flour, Snacks, Total polyphenolic content*

Taking into account the growing desire of organizations across the entire food supply chain to enhance the sustainability of their operation, different opportunities and challenges for by-product valorization through extrusion processing are revealed. When incorporating by-products such as grape pomace, a rich source of bioactive compounds with different free radical scavenging activity, into extruded snacks, one of the challenges is to ensure nutritional and functional value. Extrusion cooking, one of the most versatile and efficient food processing technologies, impacted the quality of the product. Thus, the aim of this study was to evaluate and compare the effects of the enrichment with various quantities of grape pomace, whole and seedless, from white and red grape varieties, on the nutritive and functional values of the extrusion mixtures and extruded snacks. The Total phenolic content and antioxidant activity of the extrusion mixtures and extruded samples with different grape pomace percentages (10 - 40%) were evaluated. The results showed that the mixtures' antioxidant activity increased with levels of grape pomace increase, revealing its strong antioxidant activity. The extrusion process caused a decrease in extrudates' antioxidant activity compared to that of the mixtures. This fact could be explained by some factors of the extrusion process, such as screw speed and temperature which have a negative influence on bioactive compounds, thus decreasing the phenolic compounds from snacks [1]. In addition, the depolymerization of heat-labile phenolic and phenolic compounds can be explained by the loss of bioactive compounds during the extrusion cooking [2]. Even if the extrusion cooking lowered the mixtures' antioxidant activity, adding grape pomace had a positive influence on the antioxidant activity compared to the maize control. From the nutritional point of view, overall, the maize extrudates' antioxidant activity increased with the increase of grape pomace levels, leading to snack products enriched in bioactive compounds.

Acknowledgements

This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS - UEFISCDI, project number PN-III-P4-PCE-2021-0718, within PNCDI III.

References

[1] S. Mironeasa, I. Coţovanu, C. Mironeasa, M. Ungureanu-Iuga, A Review of the Changes Produced by Extrusion Cooking on the Bioactive Compounds from Vegetal Sources, Antioxidants 12 (2023) 1453.

[2] E. Šárka, M. Sluková, S. Henke, Changes in phenolics during cooking extrusion: A review, Foods 10(9) (2021) 2100.

Compliance with Current Regulations on Allergens and Hazardous Compounds in Hydroalcoholic Gels

PSB-25

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Keywords: *Gas chromatography, Hydroalcoholic gels, Personal care products, Solid phase microextraction, Tandem mass spectrometry*

Due to COVID-19, hydroalcoholic gels or hand sanitisers have become the primary strategy to mitigate its transmission and infection. Depending on their use, hand sanitisers can be classified as biocides or as cosmetic products (borderline products). Those designed to disinfect hands are considered biocides and are subject to Biocidal Products Regulation (EU) No 528/2012; while those whose purpose is cleaning or cleansing the skin are considered cosmetics and must comply with the Cosmetics Regulation (EU) No 1223/2009. The WHO published a protocol to homogenise the hydroalcoholic gel formulation and fabrication, assuring their antimicrobial properties. This protocol does not recommend the addition of other ingredients that are not specified in these formulation [1,2].

Therefore, the aim of this work was to determine sixty personal care products frequently found in cosmetic formulations, including fragrance allergens, synthetic musks, preservatives, and plasticisers, in hydroalcoholic gels and evaluate their compliance with the current regulation. A simple and fast analytical methodology based on solid-phase microextraction followed by gas chromatography – tandem mass spectrometry (SPME-GC-MS/MS), which was previously optimised [3], was validated and applied to 67 real samples. Among the 60 target compounds, 47 were found in the analysed hand sanitisers and do not comply with the WHO recommendations. In **Figure 1**, the frequency of the target compounds by families is shown and the numbers indicate how many hydroalcoholic gels samples out of the 67 analysed contain each compound. Moreover, 61% of the hydroalcoholic gels contain at least one compound that is prohibited by the Cosmetics Regulation. These results demonstrate the need for control over the formulations of these frequently used cosmetic products to ensure consumer safety without causing undesirable side effects.

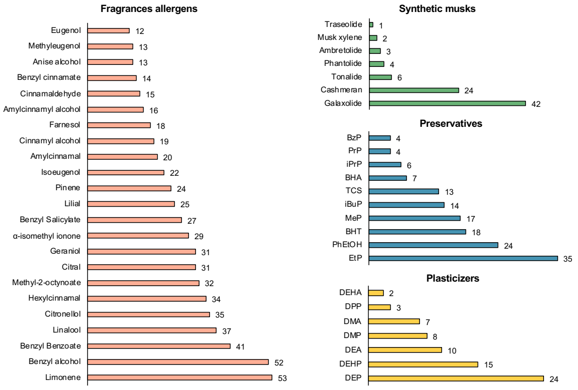

Figure 1. Frequency of the target compounds by families in the hydroalcoholic gels.

Acknowledgements
The current investigation received financial support from the projects ED431 2020/06, ED431 2023/04, IN607B 2022/15, UNST10-1E-491 and scientific support from PID2022-139874OR-C22. This research is based on the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society. Some of the authors are affiliated with the National Network for Sustainable Sample Preparation, RED2022-134079-T (Ministry of Science, Innovation and Universities, Spain). M.C. and M.L. acknowledge the IUPAC project 2021-015-2-500: Greenness of official standard sample preparation methods. A.C.L. acknowledges the Xunta de Galicia predoctoral contract (ED481A and IN606A). Special thanks to Scientific Committee of the 3rd European Sample Preparation Conference (EuSP2024) for awarding me a scholarship to attend the EuSP2024.

References

[1] World Health Organization. Guide to Local Production: WHO-Recommended Handrub Formulations. 2010. Available online: https://www.who.int/publications/i/item/WHO-IER-PSP-2010.5.

[2] European Commission. Guidance on the Applicable Legislation for Leave-on Hand Cleaners and Hand Disinfectants (Gel, Solution, etc.). Available online: https://ec.europa.eu/docsroom/documents/40523.

[3] L. Vazquez, M. Celeiro, A. Castiñeira-Landeira, T. Dagnac, M. Llompart, Development of a solid phase microextraction gas chromatography tandem mass spectrometry methodology for the analysis of sixty personal care products in hydroalcoholic gels—hand sanitizers—in the context of COVID-19 pandemic, Anal. Chim. Acta 1203 (2022) 339650.

Metabolome Diversity of Nine Apiaceae Fruits and their Anti-Cellulite Potential

PSB-26

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Keywords: *Anti-cellulite, Antioxidant, Apiaceae. Molecular networking, Untargeted metablomics.*

Apiaceae fruits are traditionally used for cosmetic applications, yet their anticellulite potential was not examined previously. In this research, nine Apiaceae fruits were selected to assess their anti-cellulite potential in parallel to mapping their constitutive secondary metabolome via untargeted mass-based metabolomics and feature based molecular networking (FBMN). In total, 260 metabolites were annotated with the aid of the FBMNs and the *in silico* fragmentation trees proposed by Sirius. Among the annotated metabolites, 25 features were tentatively assigned as new derivatives, including indole glycosides, acylated flavonoids, acylated cinnamic acids, sulfated cinnamic acids, acylated coumarins and chromones, acylated stilbenes, sulfated chalcone, and acylated xanthone. Acylated flavonoids and coumarins were distinctive for *Ammi majus*, while sulfated and acylated cinnamic acids were distinguishing for *Petrosilinum crispum*, and stilbenes were unique for *Foeniculum vulgare*. Regarding the antioxidant and anti-cellulite potential of the selected Apiaceae fruits, *Apium graveolens,* and *Petroselinum crispum* revealed potent free radical scavenging activity and in vitro anticellulite properties. Correlating the observed activities with the underlying metabolomes via hierarchical and biologically layered FBMN revealed differential flavone derivatives, including a flavone (apigenin) and a methoxyflavone (diosmetin) as well as glycoside derivatives (apigenin-O-pentosyl hexoside and apigenin-O-hexoside) as key metabolites in *A. graveolens* and *P. crispum*.

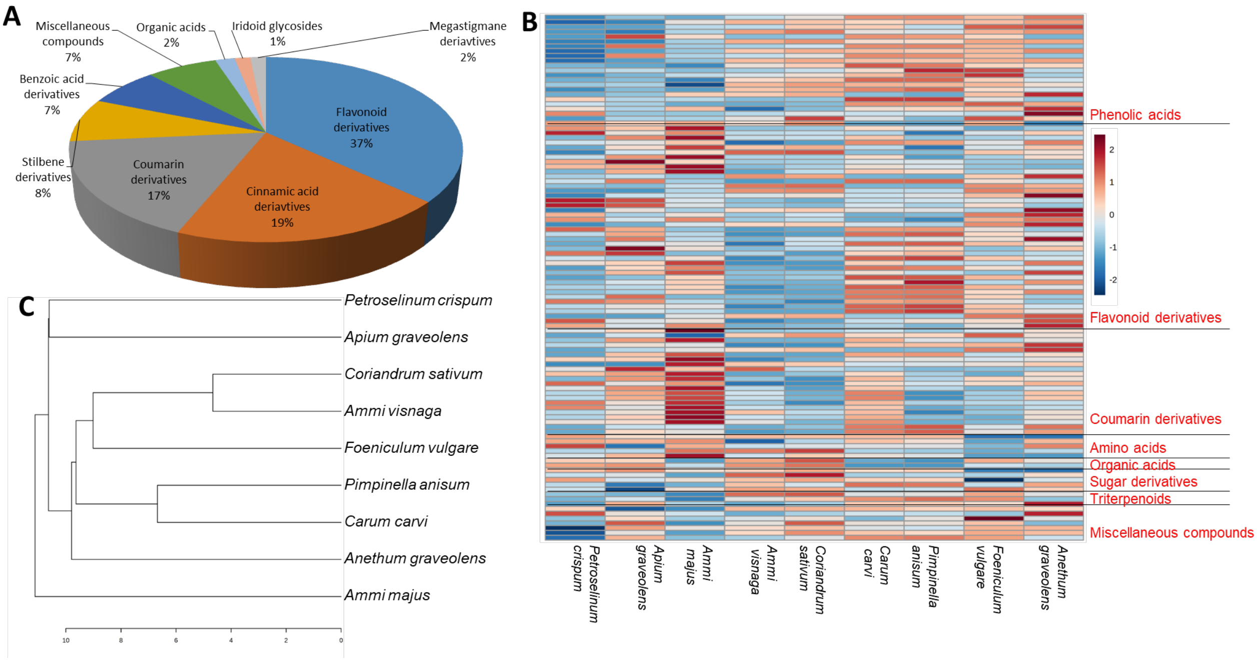

Figure 1. Classification (A), levels (B) and hierarchical clustering (C) of identified metabolites based on LC-MS analysis of tested Apiaceae fruits.

Synthesis and Characterization of Aptamer-Modified Hybrid-Silica Monolithic Capillary for Extraction of Amyloid Peptides

PSB-27

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Keywords: *Aptamer, Biomarker, Biological samples, HPLC-MS/MS, In-tube SPME*

The cerebrospinal fluid (CSF) biomarkers amyloid-β peptides 42 (Aβ42), total Tau (T-tau) and Tau phosphorylated at threonine 181 (P-tau181) have proven diagnostic accuracy for mild cognitive impairment and dementia due to Alzheimer's Disease (AD) [1]. Among these biomarkers, the concentration ratio between the two amyloid-β peptides Aβ42 and Aβ40 (Aβ42/40 ratio) has been suggested to be superior to the concentration of Aβ42 alone when identifying patients with AD. The Aβ peptide quantitation remains challenging because they are present at extremely low endogenous concentrations, tend to aggregate, and undergo nonspecific binding to surfaces and albumin, not to mention that matrix effects are introduced during electrospray ionization (ESI) [1]. Thus, developing new sample preparation strategies that can effectively clean up the extract from endogenous interferences and preconcentrate the analytes before HPLC-MS/MS analysis is important. Aptamers are single-stranded oligonucleotides usually between 20 and 100 bases long and may have, like antibodies, a specificity toward a ligand (small organic molecules, peptides, nucleic acids, proteins, intact cells) [2]. Due to their high specificity, aptamer-based SPE sorbents, named oligosorbents, have recently been reported in the field of sample preparation [2]. Furthermore, these selective sorbents have shown very promising results and advantages compared to immunosorbents. In this study, a capillary oligosorbent (530 µm inner diameter and 100 mm length) was prepared. This selective extraction capillary combined the characteristics of a hybrid-inorganic silica monolith such as high surface area, high permeability, and biocompatibility as support with the high extraction mechanism of aptamers to enrich peptides Aβ. In the first step, the synthesis of the monolithic support was optimized using tetraethoxysilane and 3-aminopropyltriethoxysilane as precursors, cetyltrimethylammonium bromide as mesoporous template, and ethanol as solvent. Scanning electron microscopic characterization confirmed that the monolith was successfully attached to the internal capillary surface. Next, the surface of the monolith was grafted by a 5′-amino-modified Aβ aptamer with a C12 spacer arm (**Figure 1**). The coverage density of the Aβ aptamers covalently immobilized on the monolith was very high and reached 655+15 pmol μL^{-1}. The capillary extractions were carried out in offline mode and important parameters were optimized (volume and composition of the different washing and elution steps) to achieve the best selective extraction capabilities and minimize the matrix effect of the binding buffer (BB) that could occur during HPLC-MS/MS analysis. The final extraction condition on the monolithic oligosorbent was able to extract Aβ40 (extraction recovery ~80 %) and Aβ42 (extraction recovery ~45 %) when binding buffer spiked with the targeted analytes was percolated. In ongoing studies, we are evaluating different monolithic oligosorbents coupled online to the HPLC-MS/MS system to carry out online extraction and determination. Once developed, the online method will be validated and used to determine Aβ in CSF sample as a biomarker for AD.

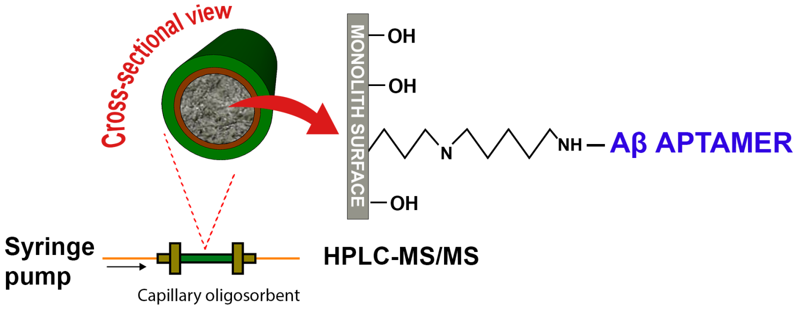

Figure 1. Extraction capillary with the Aβ aptamers grafted onto a hybrid-silica monolithic support.

Acknowledgements
This work was supported by grants from Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001 - under CAPES/COFECUB program (processes 88881.711934/2022-01, 88887.892923/2023-00, and Ph-C 988/23) and Instituto Nacional de Ciência e Tecnologia Translacional em Medicina (INCT-TM) (process 465458/2014-9).

References

[1] I.D. Souza, M.E.C Queiroz, Advances in sample preparation and HPLC–MS/MS methods for determining amyloid-β peptide in biological samples: a review. Anal. Bioanal. Chem. 415 (2023) 4003–4021.
[2] V. Pichon, Aptamer-based and immunosorbents in Solid-Phase Extraction, Elsevier, 2020, pp. 151–183.

Voltammetric Procedure for the Determination of Ce(III) in Environmental Waters Utilizing Accumulation on an Multi-Walled Carbon Nanotubes Modified Screen-Printed Electrode

PSC-01

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Keywords: *Cerium, Determination, Environmental waters, Voltammetric method*

Today, almost nothing works without rare earth metals. There would be no smartphones, flat screens, LED lights, batteries, electric motors and many other electronic devices. It is therefore of increas-ing interest to find out where these rare earth elements get into after use. When analysing wastewater from industrialised areas, it was noted that of the rare earth elements, the highest concentrations were found for cerium. The scientists therefore assume that in the near future elevated concentrations of cerium will also be found in lakes, rivers and groundwater [1,2]. Therefore, the aim of our research was to develop a voltammetric procedure that allows the determination of Ce(III) in environmental waters. The main advantages of voltammetric procedures are, first and foremost, the low cost of the apparatus, the possibility of taking measurements in the field and, very importantly, the possibility of obtaining very low detection limits. The procedure of voltammetric cerium determination in the presence of Alizarin S and acetate buffer was employed as the initial method. The adsorption material, multi-walled carbon nanotubes (MWCNTs), was used as a screen-printed carbon electrode (SPCE) modifier ensuring efficient accumulation of the Ce(III)-Alizarin S complex. The calibration graph for Ce(III) for an accumulation time of 60 s was linear in the range from 1×10^{-8} to 7×10^{-7} mol L^{-1} with the linear correlation coefficient $r = 0.997$. The detection limit estimated from 3 times the standard deviation of low Ce(III) concentration and an accumulation time of 60 s was about 3.5×10^{-9} mol L^{-1}. The developed method for the MWCNTs/SPCE used as an electrochemical sensor was further applied to the determination of Ce(III) in environmental water samples. The samples were spiked with known amounts of Ce(III) at 5×10^{-8} mol L^{-1} level, followed by voltammetric analysis of these samples to determine the sensitivity and accuracy of the applied MWCNTs/SPCE. Recoveries obtained for the river water, lake water and rain water samples ranged from 93% to 98%. The results demonstrated the applicability of the MWCNTs/SPCE for direct analysis of real samples without any pretreatment [3].

References

[1] V. Balaram, Advances in analytical techniques and applications in exploration, mining, extraction, and metallurgical studies of rare earth elements, Minerals 13 (2023) 51.
[2] T. Behrsing, V.L. Blair, F. Jaroschik, G.B. Deacon, P.C. Junk, Rare Earths—The answer to everything, Molecules 29 (2024) 688.
[3] M. Grabarczyk, M. Fialek, E. Wlazlowska, A convenient strategy for the voltammetric direct determination of Ce(III) in environmental waters using a multi-walled carbon nanotubes modified screen-printed carbon electrode. Molecules 29 (2024) 1198.

Cathodic Stripping Voltammetry Using a Solid Bismuth Microelectrode for the Determination of Trace Amounts of Se(IV) in Environmental Waters

PSC-02

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Keywords: *Bismuth microelectrode, Determination, Environmental waters, Selenium, Voltammetric method*

Electrochemical methods play a significant role in trace element analysis not only because of their high sensitivity and selectivity, but also because of their ease of use, cost-effectiveness, and possibility of speciation analysis. Of the electrochemical methods, stripping analysis is the most sensitive technique with detection limits in the ppb and sub-ppb range. This method allows the determination of Se(IV), which is the electrochemically active form, in contrast to Se(VI). In our research on selenium speciation, we focus on developing a procedure using a solid bismuth microelectrode that would allow for the determination of the lowest concentrations of Se(IV) and could be used for field analysis. Microelectrodes offer a number of advantages, such as spherical diffusion so that measurements can be made from unmixed solutions, which simplifies the measurement procedure and enables field analysis, the small size of microelectrodes enables analysis of small-volume samples, and they have a more favourable signal-to-noise ratio. All of the above advantages are provided by the solid bismuth microelectrode recently developed in our research group, which has so far been applied to the determination of both organic compounds (folic acid) [1] and inorganic ions (Tl(I), W(VI), Sn(II) and Ga(III)) [2-5].

The current research work is an attempt to analyze selenium(IV) ions in environmental water samples using an eco-friendly miniaturized sensor developed by placement very tiny amount of metallic bismuth in a tightly closed miniaturized housing. Numerous experimental variables are optimized, including the composition of the supporting electrolyte and its pH as well as activation and accumulation conditions. Under optimized measurement conditions, the method shows high sensitivity, permitting a very low limit of detection equal to 7×10^{-10} mol L^{-1} to be achieved in a short accumulation time of 50 s. A series of voltammetric experiments were carried out and they proved that the miniaturized sensor used is characterized by very good precision as well as long-term stability. The selectivity of the solid bismuth microelectrode to Se(IV) was examined in the presence of miscellaneous metal ions and Triton X-100. As has been proven, Triton X-100 occurring in the concentration range from 0.2 to 2.0 mg L^{-1} has a similar impact on the analytical signal as surfactants in natural waters. Hence, the impact of 2 mg L^{-1} of Triton X-100 on the 1×10^{-8} mol L^{-1} Se(IV) voltammetric signal was studied and turned out to be irrelevant. As for the influence of other cations, it was found that at least a 100-fold excess of Co(II), Cr(III), Cr(VI), Fe(III), Ga(III), Ge(IV), Hg(II), Mn(II), Ni(II), Pb(II), Pt(IV), Sb(III), Sn(II), V(V), and Zn(II) is tolerable within an error of ±5%, while a 10-fold excess of Cd(II) and Cu(II) causes the selenium peak to be reduced by 50%. It has also been shown that the solid bismuth microelectrode exhibits a good voltammetric response in the analysis of environmental waters with a complex matrix and shows a good recovery factor [6].

References

[1] I. Gęca, M. Korolczuk, Sensitive Determination of Folic Acid using a Solid Bismuth Microelectrode by Adsorptive Stripping Voltammetry, Electroanalysis 32 (2020) 496.
[2] I. Gęca, M. Ochab, M. Korolczuk, Anodic Stripping Voltammetry of Tl(I) Determination with the Use of a Solid Bismuth Microelectrode, J. Electrochem. Soc. 167 (2020) 086506T.
[3] M. Adamczyk, M. Grabarczyk, W. Leszko, A voltammetric approach to the quantification of tungsten in environmental waters using a solid bismuth microelectrode, Measurement 194 (2022) 111089.
[4] M. Adamczyk, M. Grabarczyk, Application of a Solid Bismuth Microelectrode in an Adsorptive Stripping Voltammetric Procedure of Trace Tin Quantification, J. Electrochem. Soc. 169 (2022) 016515.
[5] M. Grabarczyk, E. Wlazlowska, An Activated Bismuth Layer Formed In Situ on a Solid Bismuth Microelectrode for Electrochemical Sensitive Determination of Ga(III), Membranes 12 (2022) 1267.
[6] M. Grabarczyk M. Fialek, Microelectrode voltammetric analysis of low concentrations of Se(IV) ions in environmental waters. Molecules 29 (2024) 1583.

A Synergistic Approach for the Co-Production of Hydrogen and Nanocarbon from Plastic Waste via Thermo-catalytic Route

PSC-03

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Keywords: *Catalyst, Hydrogen, Nanocarbon, Plastic waste, Pyrolysis*

The production of plastic waste, coupled with inadequate recycling rates, has reached alarming levels. Thermo-chemical transformation of carbonaceous waste, such as plastics, emerges as a promising technology and a viable avenue to extract resources in contrast to conventional waste management methods like incineration and landfilling. Pyrolysis and further catalytic reforming results in the production of hydrogen and carbon intermediates in the form of carbon nanotubes. Thermo-catalytic conversion of plastic waste to hydrogen is an innovative approach for addressing growing concerns of plastic pollution and the need for sustainable energy sources. Ni/Al_2O_3 and Fe/Al_2O_3 catalysts were prepared via wet impregnation method. Concentration of hydrogen in case of Fe catalyst was slightly higher than nickel. In case of nickel catalyst, more amount of higher hydrocarbons and methane left the system unreacted due to encapsulation of metallic Ni by carbon deposits and fast deactivation of metallic active phase associated with sintering. XRD of spent catalysts indicated significant formation of carbon on the catalysts surface. BET surface area analysis of Fe/Al_2O_3 and Ni/Al_2O_3 catalysts demonstrate type II isotherm, indicating the prevalent existence of mesopores and macropores. H3 hysteresis loops were noted at relative pressures ranging from 0.6 to 0.9, indicative of slit-shaped pores formed by the accumulation of particles. XRD analysis of Ni/Al_2O_3 show presence of peaks corresponding to $NiAl_2O_4$ and small peaks of NiO. XRD of calcined Fe/Al_2O_3 show presence of peaks associated with Fe_2O_3 and Al_2O_3. Raman spectra also served to characterize the deposited carbon product. I_D/I_G ratio in case of Ni catalyst was higher with a value of 1.37 which confirms higher degree of graphitization while I_D/I_G ratio for Fe catalyst was 1.24. $I_{G'}/I_G$ ratio is higher in case of Fe catalyst than Ni which favours higher purity of deposited carbon. Carbon deposition was further evident from SEM and TEM images, indicated by the presence of filamentous carbons with a dense covering seen on the nickel catalyst surface with most of the deposition being crooked or entangled. Thus, thermo-catalytic conversion of plastic waste to hydrogen is an innovative approach for addressing growing concerns of plastic pollution and the need for sustainable energy sources.

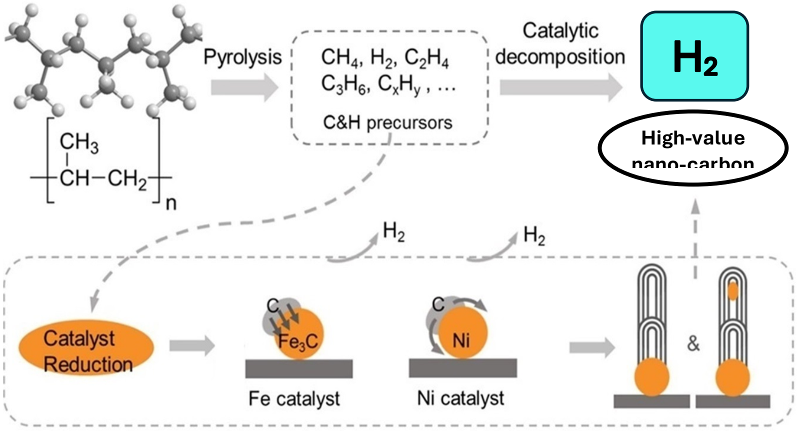

Figure 1. Pyrolysis and catalytic decomposition mechanism.

Acknowledgements
Abdul Rafey acknowledges the Prime Minister Research Fellowship Scheme, Ministry of Education, Government of India and Indian Institute of Technology Delhi.

References

[1] A. Rafey, K. Pal, A. Bohre, A. Modak, K.K. Pant, A state-of-the-art review on the technological advancements for the sustainable management of plastic waste in consort with the generation of energy and value-added chemicals, Catalysts 13 (2023) 1-24.
[2] P.T. Williams, Hydrogen and Carbon Nanotubes from Pyrolysis-Catalysis of Waste Plastics: A Review, Waste and Biomass Valorization 12 (2021) 1-28.
[3] Y. Zhang, Z. Fu, W. Wang, G. Ji, M. Zhao, A. Li, Kinetics, product evolution, and mechanism for the pyrolysis of typical plastic waste, ACS Sus. Chem. and Eng. 10 (2022) 91-103.

Development of Analytical Green Methodologies for the Detection of Contaminants of Emerging Concern

PSC-04

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Keywords: *CECs, Green sample preparation, HS-SPME, Lyophilization*

In recent years, contaminants of emerging concern (CECs) have garnered increasing attention due to their persistent and potential toxicity in various ecosystems, having significant threats to the environment and human health [1]. This increasing awareness of CECs has driven the scientific community to develop technologies for their separation and detection. The most common techniques for separation include gas chromatography (GC) or liquid chromatography (LC), meanwhile high-resolution mass spectrometry (HRMS) or tandem mass spectrometry (MS/MS) are used for their detection.

As the CECs' concentrations in the environment are not sufficiently high to be detected directly, the samples must undergo a pre-treatment phase before detection, which includes, pre-concentration and purification. Depending on the nature of the substance to be examined, the commonly used pretreatment methods are solid phase extraction (SPE), liquid-liquid extraction (LLE), solid-liquid extraction (SLE) [2]. Unfortunately, these typical sample preparation methodologies entail the use of large amount of organic solvents that are dangerous to the environment [3]. Therefore, it is crucial to develop analytical methods that can selectively and sensitively control and monitor the presence of these compounds in various environmental compartments, but at the same time ensuring that these methods are sustainable, minimizing the use of toxic and dangerous substances, reducing the waste and ensuring the operator safety.

Hence, this work presents two novel, economical, and environmentally sustainable analytical methods for extraction, preconcentration, and analysis of CECs from water and snow samples using headspace (HS)-solid-phase microextraction (SPME) and freeze-drying. These two methods have emerged as alternative techniques, offering the minimum use of solvents and enhancing the detection limit of compounds by concentrating and isolating them from complex matrices while minimizing the risk of false negative [1,4]. This study explores the application of these green technologies, for the analysis and detection of volatile and non-volatile CECs in snow, river and ponds water samples from various regions worldwide. By employing the minimum use of solvent during the extraction and detection, it is aimed to reduce the ecological footprint of environmental monitoring practices.

These processes, ranging from pre-concentration and extraction to chromatography and mass spectrometry, have allowed to identify and quantify a wide range of chemical compounds, from commonly known contaminants to emerging and less-studied ones. In summary, this work affords a multidisciplinary and global approach to understand and address the challenges associated with water and snow pollution in various parts of the world. From initial sampling to detailed chemical analysis and advanced experimentation, each step has contributed to expanding the knowledge and finding innovative solutions to protect and preserve our natural water resources. Lastly, this study not only provides a comprehensive assessment of CECs but also underscores the potential of green technologies to enhance environmental sustainability in analytical chemistry.

Acknowledgements

This research was supported by, funded by the European Union under the Marie Skłodowska-Curie Actions (MSCA) – Doctoral Network- IN2AQUAS (grant agreement No 101119555) and MSCA-Research and Innovation Staff Exchange SusWater (grant agreement No 101007578).

References

[1] Z. Yiqing, G. Shanshan, S. Qian, Research Progress on Lyophilization for Pretreatment of Emerging Organic Contaminants in Environmental Samples, Chinese Journal of Chromatography (Se Pu) 39(8) (2021) 827–834.
[2] S. Shyamalagowri, N. Shanthi, J. Manjunathan, M. Kamaraj, A. Manikandan, J. Aravind, Techniques for the Detection and Quantification of Emerging Contaminants, Physical Sciences Reviews 8(9) (2023) 2191–2218.
[3] N. Winterton, The Green Solvent: A Critical Perspective, Clean Tech. and Env. Policy 23 (2021) 2499–2522.
[4] X. He, B. Majid, H. Zhang, W. Liu, M.A. Limmer, J.G. Burken, H. Shi, Green Analysis: Rapid-Throughput Analysis of Volatile Contaminants in Plants by Freeze-Thaw-Equilibration Sample Preparation and SPME-GC-MS Analysis, J. Agric. Food Chem. 69(18) (2021) 5428–5434.

Sustainable Biocatalysis: Exploiting Hemp Waste for Lipase Immobilization and Oleic Acid Esterification

PSC-05

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Keywords: *Adsorption, Circular economy, Hemp waste, Lipase immobilization, Oleic acid esters*

Catalysts play a crucial role in various industries, including chemicals, pharmaceuticals, fuels, and energy production. Traditional synthetic chemical catalysts often require harsh conditions and complex processes [1]; on the other hand enzymatic catalysis offers a more environmentally friendly alternative, as it can occur at lower temperatures and in water-based solutions, reducing the need for hazardous chemicals [2].

Despite their advantages, free enzymes have limitations such as low stability and poor reusability. To overcome these challenges, immobilizing enzymes on solid supports has become more and more popular [3]. This approach offers several benefits, including easier product isolation, catalyst recycling, and cost-effectiveness.

In today's world, where circular economy and bioeconomy principles are gaining traction, recycling and reusability are crucial for sustainable development. Insoluble biocatalysts, especially when derived from agro-industrial waste like mesoporous lignocellulosic materials, represent a viable alternative to chemical catalysis. By utilizing waste materials as enzyme supports, is possible not only to mitigate environmental burdens associated with waste disposal but also contribute to the development of resource-efficient bioprocessing technologies [4,5].

Considering the above, the primary objective of this study was to immobilize lipase from *Candida rugosa* onto hemp wastes through physical adsorption. The aim was to understand how the characteristics of the solid biocatalyst vary based on the type of hemp waste used as a carrier, such as hemp tea waste (HTW), hemp leaves (HL), and hemp flowers (HF). The goal was to create a solid biocatalyst that effectively retained the enzyme while maintaining high catalytic activity for producing oleic acid esters.

In addition, esters like decyl oleate have become increasingly important not only in the cosmetics and personal care products industry for their excellent lubricating properties and low viscosity, but also in the production of biofuels and many other commonly used products [7,8]. They serve principally as essential emollients and conditioning agents in various cosmetics and personal care products, so are produced in enormous quantity every year. Their large production has led to the need to create new and more environmentally friendly industrial synthesis methods. One way to do this is certainly the development of solvent-free methods.

The adoption of a solvent-free system in the production of oleic acid esters holds significant importance in recent decades for several compelling reasons [6]. Firstly, the elimination of solvents reduces human health and environmental impact by minimizing the release of volatile organic compounds. Moreover, solvent-free systems offer economic advantages by reducing operating costs associated with solvent procurement, handling, and disposal. In contrast, solvent-free methodologies streamline production processes, leading to cost savings and improved resource efficiency. Additionally, solvent-free systems enhance product purity and quality by eliminating the need for solvent removal steps, which can introduce impurities and compromise product integrity. This is particularly significant in industries such as cosmetics and pharmaceuticals, where product purity is crucial.

Overall, the utilization of solvent-free systems in the production of oleic acid esters offers a holistic approach to sustainable manufacturing, integrating environmental, economic, and quality considerations, especially if coupled with biocatalysis carried on by enzyme immobilized on recycled and biocompatible supports like hemp wastes. By prioritizing biocompatible methodologies like the one presented, industries can achieve significant improvements in efficiency, safety, and environmental performance, paving the way for a more sustainable future.

Acknowledgements

This work was funded by the project 2022 RM12117A5D872C39 (Principal Investigator M.L. Astolfi) financed by Sapienza University of Rome.

References

[1] S. Donzella, M.L. Contente, The joint effort of enzyme technology and flow chemistry to bring biocatalytic processes to the next level of sustainability, efficiency and productivity, J. Flow Chem. (2023).
[2] B. Hauer, Embracing Nature's Catalysts: A Viewpoint on the Future of Biocatalysis, ACS Catal. 10 (2020) 8418–8427.
[3] Y.R. Maghraby, R.M. El-Shabasy, A.H. Ibrahim, H.M.E.S. Azzazy, Enzyme Immobilization Technologies and Industrial Applications, ACS Omega 8 (2023) 5184–5196.
[4] R. Nattassha, Y. Handayati, T.M. Simatupang, M. Siallagan, Understanding circular economy implementation in the agri-food supply chain: the case of an Indonesian organic fertiliser producer, Agric. Food Secur. 9 (2020) 1–16.
[5] S. Yu, J. Sun, Y. Shi, Q. Wang, J. Wu, J. Liu, Nanocellulose from various biomass wastes: Its preparation and potential usages towards the high value-added products, Environ. Sci. Ecotechnology 5 (2021) 100077.
[6] R.R. Sousa, A.S.A. Silva, R. Fernandez-Lafuente, V.S. Ferreira-Leitão, Solvent-free esterifications mediated by immobilized lipases: A review from thermodynamic and kinetic perspectives, Catal. Sci. Technol. 11 (2021) 5696–5711.
[7] N.R. Khan, V.K. Rathod, Enzyme catalyzed synthesis of cosmetic esters and its intensification: A review, Process Biochem. 50 (2015) 1793–1806.
[8] N.R. Khan, V.K. Rathod, Microwave assisted enzymatic synthesis of speciality esters: A mini - review, Process Biochem. 75 (2018) 89–98.

Solvent-Free Reactions as a Key to the Synthesis of Organoboron Compounds

PSC-06

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Keywords: *Borasiloxanes, Boronic esters, Solvent-free, Hydroboration, O-Borylation*

Functional boron compounds belong to a group of unique reagents that, due to their versatile properties, serve as valuable building blocks in organic synthesis and polymerization. Hydroboration and O-borylation reactions remain among the most important pathways for atomically efficient synthesis of organoboranes. The hydroboration reaction involves the addition of the B-H bond from boranes to multiple bonds in unsaturated organic compounds. This process is commonly employed for the modification of double and triple bonds into various functional groups, owing to the numerous available methods for transforming organoboranes. The significance of boron compounds in organic synthesis has led to the continuous development of hydroboration reactions, exploring new reagents, potential applications, and efficient/selective catalysts for the process. The reduction of carbonyl derivatives through hydroboration allows for the synthesis of functionalized alcohols, making this method particularly intriguing. On the other hand, the O-borylation process is a common method in the synthesis of poly(borosiloxanes), which exhibit unique and valuable properties, including high stability and heat resistance. In both cases, the majority of developed procedures are based on catalytic processes and utilize transition metal complexes, main group catalysts, and Lewis acid/Lewis base pairs. Therefore, the prospect of synthesizing these products in accordance with the principles of green chemistry has become a highly interesting challenge.

In light of these facts, in the communication, we present our methods for hydroboration and O-metalation, which proceed without the involvement of any solvents. The absence of solvents has not only allowed the development of new, efficient methods under mild conditions but importantly, also without the use of any catalysts.

Acknowledgements

Funding acknowledgement: National Science Centre Grant: UMO-2018/30/E/ST5/00045.

References

[1] Y. Wu, C. Shan, J. Ying, J. Su, J. Zhu, L. L. Liu and Y. Zhao, *Green Chem.*, 2017, 19, 4169–4175.
[2] K. Kuciński, H. Stachowiak-Dłużyńska, G. Hreczycho, *Coord. Chem. Rev.* 2022, *459*, 214456–214497.
[3] R. L. Melen, Chem. *Soc. Rev*. 2016, 45, 775–788.
[4] H. Stachowiak, J. Kaźmierczak, K. Kuciński, G. Hreczycho *Green Chem.* 2018, *20*, 1738–1742.
[5] K. Kuciński, G. Hreczycho, *ChemSusChem* 2017, 10, 4695–4698.

Reusing and Recycling 3D Printed Devices Coated with Solid-Phase Extraction Resin for Extraction of Antidepressants in Water: Towards a Truly Sustainability

PSC-07

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Keywords: *Coated 3D devices, Reusability, Recyclability, Solid phase extraction*

In few years, 3D printing has received unprecedented level of interest and attention in the field of analytical chemistry due to its capability for rapid prototyping, decreased fabrication time, one-step fabrication, and ever-increasing palette of functional print materials [1]. Among 3D printing technologies, fused deposition modelling (FDM) is the most used technique due to its simplicity, low cost, and a wide variety of thermoplastic polymers [2]. Despite its advantages, 3D printing generates substantial waste. Filament material is frequently discarded due to printing failures, broken parts, filament replacements, discarded support structures, and nozzle tests. Consequently, the growth of the polymer additive manufacturing market is likely to contribute to an increase in plastic waste [3]. Therefore, this study proposes the reuse and recyclability of a 3D device for the extraction of antidepressants in water, using commercial solid phase extraction (SPE) resin, with the aim of achieving a truly sustainable methodology. A 3D device of virgin polylactic acid (PLA) was designed and printed by FDM and then functionalized with a suspension of SPE resin in polyvinylidene fluoride/dimethylformamide (PVDF/DMF). These 3D coated devices were used in addition/recovery assays of venlafaxine as model compound. Subsequently, analytical determination was performed by HPLC-DAD. The reusability of 3D coated device was established in terms of extraction efficiency (E). When E falls below 10%, the 3D coated device was chopped up and used to generate recycled PLA filament (Fig.1). With the recycled filament, recycled 3D devices were printed, coated, and used for new analyte extractions. No significant differences were observed in venlafaxine recoveries between virgin and recycled PLA 3D devices with a confidence of 95% accordingly to the t-test. As the study showed promising results for venlafaxine, other analytes such as its metabolite O-desmethylvenlafaxine are being investigated, as well as the number of cycles that 3D recycled coated device can be reused and recycled. SEM images were taken before and after impregnation and after use, for both virgin and recycled devices. This study confirms that the residues generated by 3D FDM printed devices in analytical chemistry could be reduced to be in concordance with sustainable analytical chemistry.

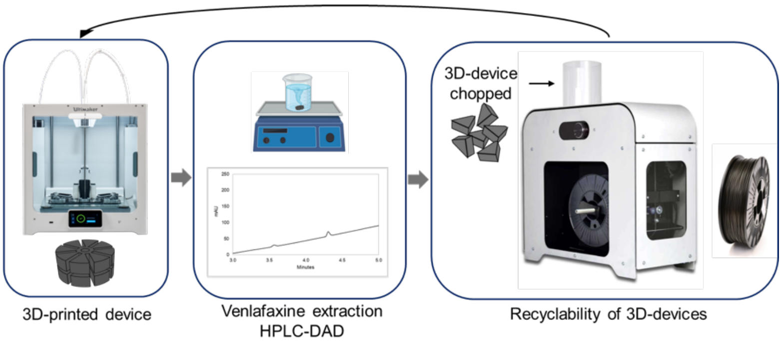

Figure 1. Overall process description.

Acknowledgements
Financial support from the Spanish Ministry of Science and Innovation, Agencia Estatal de Investigación (project PID2019-107604RB-I00/MCIN/AEI/ 10.13039/501100011033) is gratefully acknowledged. Brenda Mejía acknowledges the support from the National Council of Humanities, Sciences and Technologies, Mexico and to the Advanced Materials Research Center for the pre-doctoral research fellowship.

References
[1] H. Agrawaal, J.E. Thompson, Additive manufacturing (3D printing) for analytical chemistry, Talanta Open 3 (2021) 100036.
[2] S.A. Monteiro, C. Scheid, M. Deon, J. Merib, Fundamentals, recent applications, and perspectives of 3D printing in sample preparation approaches, Microchemical Journal 195 (2023) 109385.
[3] S. Bergaliyeva, D.L. Sales, F. J. Delgado, S. Bolegenova, S.I. Molina, Manufacture and characterization of polylactic acid filaments recycled from real waste for 3D printing, Polymers 15 (2023) 2165.

Comparison of Official Analytical Methods with Corresponding Methods Using SPME for their Greenness

PSC-08

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Keywords: *Greener sample preparation, SPME, AGREE, AGREEprep*

Many official methods from US EPA, AOAC, ASTM or ISO have been developed many years or decades ago. Due to this they are lacking modern approaches for both sample preparation as well as analysis. As a result, most of these official methods require large amounts of organic solvents for liquid-liquid or Soxhlett extraction, which poses environmental, health and hazard risks [1]. Consequently, they do not comply any longer with the today’s requirements for more sustainable practices in the lab. Methods utilizing miniaturized and solvent-free sample preparation techniques address this requirement much better.

Solid Phase Microextraction (SPME) was developed in 1990 [2] and is such miniaturized and solvent-free sample preparation technique. SPME uses fibers overcoated with polymers or particles embedded in polymers to extract organic compounds from very diverse matrices without using any organic solvent. The extraction is based on an equilibrium partitioning between the coating on a fiber and the sample matrix. The analytes are desorbed from the fibers thermally. Over the years, SPME has emerged as a powerful and versatile sample preparation technique due to its high sensitivity and selectivity and gained broad acceptance in environmental, pharmaceutical and food analysis. The popularity of this technique was further enhanced by enabling the automation of the complete sample preparation procedure using GC autosamplers in 1993. Another indication of the broad acceptance is the use of SPME in official methods and standards. Several of the features of SPME are well in alignment with the 12 principles of Green Analytical Chemistry [3] such as being a solvent-free extraction technique, which is miniaturized and can be easily automated.

This work highlights the key principles and features of SPME and focuses on various official methods in environmental testing. These methods will be compared with a corresponding method using SPME and the superior greenness of the SPME methods will be demonstrated by applying metrics for Green Analytical Chemistry [4].

References

[1] E. Psillakis, A. Chisvert, C. Cagliero, S.A. Ozkan, M. Segundo, Z. Mester, Chemistry International January-March 2024, 26 (2024).
[2] C. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[3] A. Gałuszka, Z. Migaszewski, J. Namiesnik, TrAC 50 (2013) 78.
[4] M. Sajid, J. Płotka-Wasylka, Talanta 238 (2022) 123046.

Simple and Rapid Determination of Salivary Lysozyme in Real Samples by tITP-CZE-UV

PSC-09

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Keywords: *Capillary electrophoresis, In-capillary preconcentration, Lysozyme, Saliva*

Introduction. Biomarkers have a fundamental importance in the medicine today, as they bring new possibilities for simple screening, diagnosis, and monitoring of diseases or prediction of treatment. Saliva is a good source of biomarkers, mainly because it is noninvasive and easy to collect. One potential biomarker in saliva is lysozyme, one of the most important antimicrobial proteins in the human body. The level of salivary lysozyme is closely related to several diseases, which makes salivary lysozyme an interesting biomarker candidate.

Capillary electrophoresis (CZE) is a high-throughput analytical method with high separation efficiency for analyzing both small and large molecules in complex matrices. In combination with UV detection, it provides robust, simple, and fast analytical technique suitable for detection and quantification of lysozyme in saliva. The aim of this work is to develop a CZE-UV method for the quantitative analysis of salivary lysozyme using simple UV detection.

Methods. Salivary lysozyme analyses were performed by capillary zone electrophoresis using transient isotachophoresis (tITP) as a preconcentration step. The CZE was carried out in a 75 µm I.D. uncoated fused silica capillary of 52 cm effective length. The samples were hydrodynamically injected by applying a pressure of 50 mbar for 100 s, which was possible due to the tITP preconcentration. The cationic regime of the separation was used, and a separation voltage of +15 kV was applied. UV detection was provided by a photodiode array detector.

Results. In this work, we optimized the parameters of tITP-CZE-UV for analysis of salivary lysozyme. High intensity, narrow peak shape and good separation were achieved using BGE containing 1 M formic acid with 10% isopropyl alcohol. The optimization of injecting consisted in the comparison of hydrodynamic (HDI) and electrokinetic injection in combination with and without preconcentration step (tITP). Online tITP using HDI provided the highest intensity and excellent separation efficiency with an acceptable migration time (<15 min). The adsorption of lysozyme onto the insert surface was prevented by pretreating the insert with a carrier protein, thereby enhancing the repeatability of peak areas, especially at low concentrations. Additionally, a variety of sample treatment approaches were tested, including centrifugation and simple dilution, filtration and solid-phase extraction. Validation was performed using artificial saliva matrix and an internal standard. The results showed excellent linearity (r^2=0.9997) over two orders of magnitude, acceptable intra-day precision (RSD, 1.23-4.09%) and accuracy (RE, -0.56-5.36%), and matrix effects at the level of 87.4-88.6%.

Conclusion. The optimized tITP-CE-UV method is sufficiently robust and selective to determine the lysozyme in salivary matrix without extensive sample treatment. The LLOQ of lysozyme in water and artificial saliva is 1 µg/mL, which is sufficient for the intended application, as the concentration of salivary lysozyme in healthy people ranges approximately from 10 to 70 µg/mL [1].

Acknowledgements

This work was supported by the grants UK/3181/2024, VEGA 1/0514/22 and carried out in the Toxicological and Antidoping Center at the Faculty of Pharmacy, Comenius University Bratislava.

References

[1] M.A. Kmiliauskis, P. Palmeira, C. Arslanian, G.N. Pontes, B.T. Costa-Carvalho, C.M. Jacob, M.M.S. Carneiro-Sampaio, Salivary lysozyme levels in patients with primary immunodeficiencies, Allergol. Immunopathol. 33 (2005) 65–68.

Microflow LC-MS: A Step Towards Reconciling the Reduction of Environmental Impact and Analytical Performances in the Context of Green Chromatography

PSC-10

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Keywords: *Green analytical chemistry, Greener chromatography, Microflow LC-MS, Micropollutants, Sediments*

Analytical chemistry applied to the environment constitutes a paradox. Indeed, its activities are involved in environmental protection by monitoring substances across different matrixes, such as wastewaters or sediments, while having an impact on the environment and on health due to the use of toxic reagents/solvents and high energy consumption instruments, such as liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS). This paradox gave birth to the Green Analytical Chemistry (GAC) first conceptualized in 2013 by defining 12 principles [1]. These principles include concepts such as minimizing energy consumption, reducing the quantity of solvents and reagents used or miniaturizing methods. Nevertheless, some of these principles were judged to be potentially disadvantageous from the point of view of analytical performances. It is therefore crucial to reconcile the reduction of environmental impact with analytical performances to keep on reaching our goals. This is the target of White Analytical Chemistry that was conceptualized in 2021 [2].

The aim of this work is to study the use of micro-flow liquid chromatography coupled with tandem mass spectrometry (µ-LC/MS) for the analysis of various trace and ultra-trace micropollutants in river sediments. This instrument allows to considerably reduce the quantity of solvents used during the instrumental analysis stage compared to conventional liquid chromatography by reducing the internal diameter of columns which leads to the use of lower flow rates. While µ-LC/MS is used routinely in the world of proteomics, where its use is motivated by the low quantity of sample available, it remains little used in environmental analysis. This work therefore represents a first step of the discipline towards GAC with the use of miniaturized fluidic in the instrument. In addition, this coupling promises further benefits in terms of analytical performance. Indeed, the reduction of the chromatographic dilution and the formation of smaller droplets during the ionization leads to better ionization, and thus better sensitivity, and to the reduction of matrix effects as some studies have shown [3]. Our research focuses on the development of in µ-LC/MS of a multi-residual method for the detection and the quantification of several compounds (pesticides and pharmaceuticals) for sediment analysis. Different internal diameters of column and flow rates will be tested to establish the best compromise between gain in sensibility, reduction of matrix effects and reduction of solvents consumption. Then a comparison between the µ-LC/MS and the LC/MS will be presented to identify the benefits of µ-LC/MS both from an environmental standpoint and in terms of analytical performances (repeatability, sensitivity, matrix effects, etc.).

Acknowledgements
Funded by the European Union under the GA n°101060211. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or REA. Neither the European Union nor the granting authority can be held responsible for them.

References
[1] A. Gałuszka, Z. Migaszewski, J. Namieśnik, The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices, TrAC Trends Anal. Chem. 50 (2013) 78-84.
[2] P. M. Nowak, R. Wietecha-Posłuszny, J. Pawliszyn, White Analytical Chemistry: An approach to reconcile the principles of Green Analytical Chemistry and functionality, TrAC Trends Anal. Chem. 138 (2021) 116223.
[3] A. Uclés Moreno, S. Herrera López, B. Reichert, A. Lozano Fernández, M. D. Hernando Guil, A.R. Fernández-Alba, Microflow liquid chromatography coupled to mass spectrometry-an approach to significantly increase sensitivity, decrease matrix effects, and reduce organic solvent usage in pesticide residue analysis, Anal. Chem. 87 (2018) 1018-1025.

Utilization of Caffeine as a Potential Enhancer for Heat Transfer Fluids

PSC-11

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Keywords: *Antifreeze, Caffeine, Heat transfer fluids*

Heat transfer fluids (HTFs) are integral to the functionality of various systems, including HVAC, automotive technologies, and biomedical devices. Ethylene glycol (EG) is commonly utilized as an organic solvent in these applications due to its notable thermal properties, such as high heat capacity and good thermal stability. These characteristics make EG a vital component in antifreeze and HTF solutions. However, the high viscosity and relatively low specific heat capacity of EG pose challenges to its effectiveness as an HTF.

To mitigate these limitations, water is often added to ethylene glycol. This mixture offers advantages like cost-effectiveness and environmental safety. However, drawbacks are also introduced, including increased vapor pressure and a reduced boiling point, which limit the operational temperature range of the HTF. While a water-ethylene glycol mixture is recognized for having a higher heat capacity than pure ethylene glycol, sufficient heat transfer capabilities are still lacking, necessitating larger fluid volumes and higher operational costs. Recent advancements have involved the exploration of adding nanoparticles and other non-volatile compounds to enhance the thermal conductivity of ethylene glycol. However, viscosity is often increased and the fluid's properties may be altered. Moreover, concerns regarding cost, environmental impact, and scalability have hindered widespread adoption.

A novel approach is proposed in this research: the use of caffeine as an enhancer for ethylene glycol-based HTFs. Initial findings suggest that the viscosity of ethylene glycol is not only reduced by caffeine but its heat capacity may also be increased. Beneficial thermal properties have been demonstrated by caffeine in its role in improving the thermal stability of perovskite solar cells. Additionally, environmental and economic sustainability is highlighted, particularly through potential recycling from common sources such as coffee or tea waste, presenting it as an eco-friendly and cost-effective option.

This study focuses on the investigation of the physicochemical properties of caffeine in a 35:65 molar ratio mixture of ethylene glycol and water, a common antifreeze formulation chosen for its lowest freezing point. The influence of caffeine on the structural organization and thermodynamic properties of this mixture, especially its potential as a heat transport fluid, is explored. Previous studies have revealed that the structural organization of water molecules and ethylene glycol is affected differently by caffeine [1]. Viscosity and structural order are increased by caffeine in water [2], whereas viscosity is reduced and caffeine acts as a structure-breaker in ethylene glycol. The behavior becomes more complex in a mixture of ethylene glycol and water, where the solvents' effects on caffeine's solvation and aggregation are more intricate.

The elucidation of interactions within caffeine-ethylene glycol-water mixtures is sought using molecular dynamics simulations and experimental measurements. The impact of these interactions on the fluidity and overall performance of HTFs is crucial. Insights from this study could potentially revolutionize the design and operational methodologies of heat exchangers and thermal energy storage systems, significantly enhancing energy efficiency and sustainability.

Acknowledgements
The authors would like to acknowledge the contribution of the Cost Action CA18202 “NECTAR - the Network for Equilibria and Chemical Thermodynamics Advanced Research”, the Secretariat for Higher Education and Scientific Research of the Autonomous Province of Vojvodina, Serbia (Grant No. 142-451-2545/2021-01/2), and the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Grant No. 451-03-47/2023-01/200125).

References
[1] M. Vraneš, I. Radović, S. Bikić, A. Tot, M. Kijevčanin, T.T. Borović, S. Papović, Improving ethylene glycol transport properties by caffeine-Thermodynamic and computational evidence, J. Mol. Liq. 333 (2021) 115918.
[2] M. Vraneš, J. Panić, A. Tot, S. Gadžurić, Č. Podlipnik, M. Bešter-Rogač, How does the presence of ATP affect caffeine hydration and self-aggregation?, J. Mol. Liq. 318 (2020) 113885.

An Updated Gradient PLE-SPE×HPLC-PDA System for Extraction, Fractionation, and Analysis of Valuable Compounds from Cocoa Bean Shells

PSC-12

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Keywords: *Bioactive compounds, Biorefinery, By-products, Circular economy, Green chemistry*

Cocoa (*Theobroma cacao* L.) beans are a valuable agricultural product widely used in the food industry, especially in chocolate production. However, the shells of these beans, which are by-products accounting for about 20% of their weight, contain high levels of bioactive metabolites, including phenolic compounds and methylxanthines [1]. In this context, we proposed a methodology employing a PLE-SPE×HPLC-PDA system to extract, fractionate, and analyze five metabolites of interest present in cocoa bean shells: theobromine, caffeine, catechin, epicatechin, and procyanidin B2. Hence, an optimization step employing a fractional factorial design was adopted on the PLE, analyzing the influence of temperature (60 - 120 °C), static time (0 - 20 min), and isocratic steps starting with water (0 - 10 min) and ending with ethanol (EtOH) (0 - 10 min) on the extraction of the compounds. Subsequently, an SPE step was proposed comparing Sepra™ C18-E and PoraPak Rxn RP Bulk as adsorbents to concentrate and separate the fractions in-line with the optimized PLE method. Considering the fractionation by SPE, PoraPak Rxn RP Bulk resulted in optimal results, achieving a purified fraction with 75.05±9.22% of total theobromine without the other metabolites. Regarding the reuse of the SPE, we employed an updated PLE-SPE×HPLC-PDA system containing an additional dilution pump (**Figure 1-7**) for monitoring the performance of the system in real-time, achieving at least 10 reuses. Additionally, the Conductor-like Screening Model for Real Solvents (COSMO-RS) was employed for computational analysis of metabolite × solvents and adsorbent interactions. Finally, the updated PLE-SPE×HPLC-PDA system could extract, concentrate, and fractionate bioactive compounds from cocoa bean shells. This methodology has improved the process by reducing the number of steps, adjusting the dilution of the fractions for online analysis, and reusing the SPE.

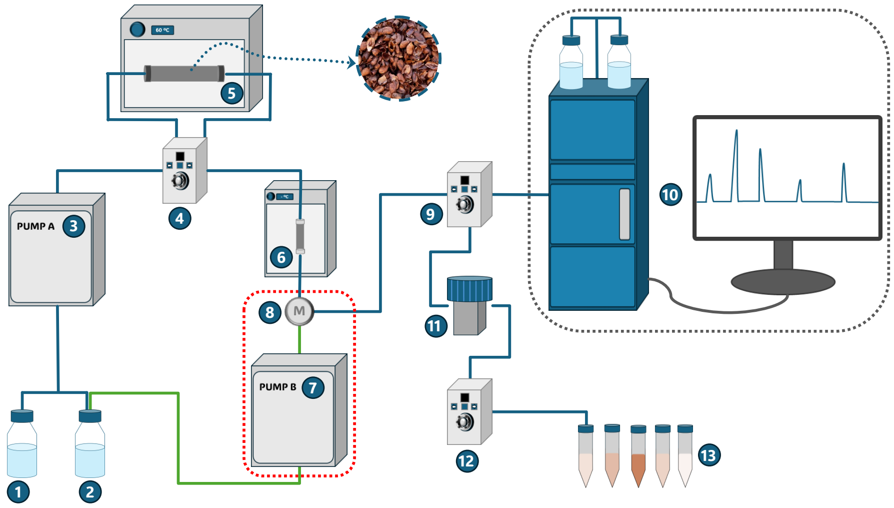

Figure 1. Schematic diagram of the updated gradient PLE-SPE×HPLC-PDA system used in this study. Ethanol reservoir (1); water reservoir (2); PLE binary pump (3); switching valve for transitioning flow to PLE-SPE or directly to SPE (4); extraction cell in the oven (5); SPE cell in the oven (6); dilution pump for pre-online analysis (7); dilution mixer (8); switching valve for filling the loop for HPLC-PDA or directly to fraction collection (9); HPLC-PDA system (10); back-pressure (11); switching valve for closing the system or collecting the fractions (12); and collected fractions (13).

Acknowledgements

The authors would like to thank the São Paulo Research Foundation - FAPESP (2023/12621-1, 2022/10469-5, 2021/12264-9, and 2018/14582-5) and the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil - CAPES (Finance Code 001).

References

[1] A. Younes, M. Li, S. Karboune, Cocoa bean shells: A review into the chemical profile, the bioactivity and the biotransformation to enhance their potential applications in foods, Crit. Rev. in Food Sci. and Nutr. 63(28) (2023).

Introduction of High Performance Liquid Chromatography Coupled to Zone Fluidics as a Versatile Approach for Derivatization Reactions

PSC-13

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Keywords: *HPLC, Post-column derivatization, Versatility, Zone fluidics*

In the present work, an alternative concept was developed to inject different reagents in High Performance Liquid Chromatography coupled to on-line Post Column Derivatization (HPLC-PCD). In classic HPLC-PCD, one suitable reagent is introduced in the flowing stream of HPLC for the derivatization of the analytes [1]. Therefore, compromise of the reaction conditions is usually used for all analytes. In the proposed concept, Zone Fluidics (ZF) configuration was applied for the introduction of different reagents in the outlet of the column, depending on the chemical system and the optimum conditions of each analyte. The reagents are introduced as well-defined volumes at microliter levels, in order to overlap the eluted compounds [2]. ZF is used for the first time after the chromatographic column, offering versatility in the selection of derivatization reactions and a more environmentally friendly HPLC-PCD approach. The development of the new HPLC-ZF-PCD system included: (1) the study of the new system for the coupling of ZF with the outlet of the column, (2) the study of the tuning of the eluted compounds with the reagent zone, (3) the study of repeatability of the new approach and (4) the development and validation of a new method using the proposed configuration. The coupling of the outlet of the column with the port of ZF was conducted through a T-connector and a zero dead-volume coupler. Different reagents were introduced in the eluent using the 10-port valve of ZF. For the development of the new system four aminothiols (homocysteine, N-acetyl-cysteine, reduced glutathione, and glutathione disulfide) were used and separated using reversed phase chromatography. The derivatization of the aminothiols was based on reaction with o-phthalaldehyde (OPA) reagent, with different chemical parameters for each analyte; (i) N-acetyl-cysteine reacts with OPA with a primary amine under the classic mechanism, (ii) reduced glutathione reacts with OPA in alkaline medium under the selective mechanism and (iii) homocysteine and glutathione disulfide react with OPA in high alkaline medium without the need of the nucleophilic compound. The tuning depended on the retention times of the analytes and the repeatability was satisfactory (RSD< 5%) using 75 μL of reagent zone. The chemical parameters of each compound were studied, and the method was validated for the determination of aminothiols in biological samples and food samples, with simple sample preparation. The development of HPLC-ZF-PCD proved to be an alternative "green" approach to post-column derivatization. HPLC-ZF-PCD was used for the determination of analytes with different reagents, without the need for compromise that is usually used in classic HPLC-PCD. In addition, the reagent consumption was dramatically reduced to 300 μL per run instead of the 7500 μL required with the HPLC-PCD approach.

Acknowledgments

The research work was supported by the Hellenic Foundation for Research and Innovation (HFRI) under the 3rd call for HFRI PhD Fellowships (Fellowship Number: 5341).

References

[1] C.K. Zacharis, P.D. Tzanavaras, Liquid chromatography coupled to on-line post column derivatization for the determination of organic compounds: A review on instrumentation and chemistries, Anal. Chim. Acta 798 (2013) 1-24.
[2] A. Tsiasioti, C.K. Zacharis, P.D. Tzanavaras, Development and evaluation of pulsed – Post column derivatization in liquid chromatography as a concept to minimize reagent consumption, J. Chromatogr. A 1690 (2023) 463791.

Pulsed – Post Column Derivatization Coupled to High Performance Liquid Chromatography: A New Concept to Minimize the Reagent Consumption

PSC-14

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***Keywords:** HPLC, Post-Column derivatization, Reduced reagent consumption*

In the present work, a new approach was developed to reduce reagent consumption in High-Performance Liquid Chromatography – Post Column Derivatization (HPLC-PCD). In HPLC-PCD, high amounts of wastes are produced due to the reagents constantly flow to react with the eluted compounds [1]. In the developed approach, the reagents are introduced as well-defined volumes of reagents - pulses (Pulsed-Post Column Derivatization, Pulsed-PCD) at microliter levels, in order to overlap the eluted compounds after precise time tuning. The development of the Pulsed-PCD system included: (1) configuration of the system, (2) study of the profiles of the injected volumes at various combinations of time and flow rates and (3) study the robustness of the system to verify its effectiveness. The proposed approach was applied for the development of three analytical methods:
(i) The determination of histidine in urine samples after derivatization with o-phthalaldehyde in alkaline medium, as a proof-of-concept.
(ii) The determination of the two closely eluted compounds, cysteine and glutathione, in yeast samples after derivatization with ethyl propiolate.
(iii) The determination of histamine in food samples after derivatization with o-phthalaldehyde and naphthalene-2,3-dicarboxaldehyde. Naphthalene-2,3-dicarboxaldehyde is an expensive reagent and has limited applications in HPLC-PCD.
The developed methods reduced the consumption of the reagents in 50-100 μL per run instead of mL required using HPLC-PCD. The determination of closely eluted compounds and the use of expensive reagents in PCD proved the effectiveness of the proposed concept and demonstrated the significant advantage of the technique over the classical technique.

Acknowledgments

The research work was supported by the Hellenic Foundation for Research and Innovation (HFRI) under the 3rd call for HFRI PhD Fellowships (Fellowship Number: 5341).

References

[1] C.K. Zacharis, P.D. Tzanavaras, Liquid chromatography coupled to on-line post column derivatization for the determination of organic compounds: A review on instrumentation and chemistries, Anal. Chim. Acta 798 (2013).

On Site Analytical Strategies to Monitor Organic and Inorganic Pollutants in Fish Farms

PSC-15

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Keywords: *Aquaculture, CECs, PTEs, Voltammetry*

Water quality, crucial for human health, ecosystem conservation, and socioeconomic development, is increasingly threatened by pollution from urbanization, industrial production, and agricultural activities. CECs and PTEs persist in the environment and are not fully removed by conventional wastewater treatment processes, leading to their accumulation in water and sediments and posing severe risks to ecosystems and human health. Aquaculture offers a promising solution to meet the growing demand for food resources [1], but it also poses significant environmental challenges due to the presence and accumulation of Contaminants of Emerging Concern (CECs) and Potentially Toxic Elements (PTEs). Due to the differing chemical and physical properties of contaminants, it is essential to understand their partitioning between water and sediments as well as the kinetics of their release from sediments. So, initially we focused on developing non-destructive sequential extraction methods to study the bioavailability and bioaccessibility of these pollutants in sediments [2].

Our research focuses on the development of innovative methods for the detection of CECs and PTEs in aquaculture waters and sediments that can be apply in situ. These electrochemical methods were initially validated in the laboratory using conventional techniques that comprise HPLC separation and atomic spectroscopy techniques.

These methods were further validated to be used in a portable detection kit, developed for on-site detection, with the aim to allow for the determination of CECs and PTEs directly in the field. The results obtained with this on-site equipment are comparable to those from laboratory hyphenated techniques. On-site analyses offer several advantages, including time and cost savings in monitoring water quality, reduced sample transport and storage needs, and more frequent evaluation of contaminant content over time.

This approach exploiting electrochemical procedures allowed us to speciate mercury and arsenic, two of the most harmful PTEs for human health. Mercury, which can bioaccumulate and biomagnify in fish, affects human health through the food chain, while arsenic and its compounds are classified as carcinogenic. Element speciation, more cost-effective than ICP-MS, and in-field analysis [2] represent the main benefits of using this analytical technique. Moreover, for mercury, speciation is crucial because methylmercury (CH_3Hg), an organometallic species, is more toxic than inorganic mercury (Hg_{in}) due to its higher lipophilicity. For this purpose, we investigated anodic stripping voltammetry using a solid gold working electrode (**Figure 1**), preceded by a preliminary separation step, necessary as both CH_3Hg and Hg_{in} oxidize at the same potential. Similarly, we developed a speciation strategy for arsenic, exploiting the much lower detection potential of As(III) than that of As(V).

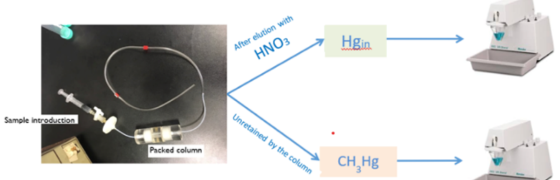

Figure 1. Scheme of the strategy adopted for the speciation of mercury.

Additionally, we addressed the on-site determination of organic CECs, such as sunscreens and pharmaceuticals, using voltammetry. This approach provides an effective and innovative environmental control tool, enhancing detection and monitoring capabilities for pollutants, and promoting more sustainable and safer aquaculture practices.

Acknowledgements
This research was supported by, funded by the European Union under the Marie Skłodowska-Curie Actions (MSCA) – Research and Innovation Staff Exchange Suswater (grant agreement No. 101007578) and MSCA-Doctoral Network-IN2AQUAs (grant agreement No. 101119555).

References

[1] D.C. Little, R.W. Newton, M.C.M. Beveridge, Aquaculture: A Rapidly Growing and Significant Source of Sustainable Food? Status, Transitions and Potential Proceedings of the Nutrition Society 75(3) (2026) 274–286.

[2] TR 117 - Understanding the relationship between extraction technique and bioavailability, ECETOC (accessed 2024-05-29). https://www.ecetoc.org/publication/tr-117-understanding-the-relationship-between-extraction-technique-and-bioavailability/.

[3] A. Giacomino, A. Ruo Redda, R. Caligiuri, P. Inaudi, S. Squadrone, M.C. Abete, O. Abollino, S. Morandi, E. Conca, M. Malandrino, Development of an Easy Portable Procedure for On-Site Determination of Mercury and Methylmercury, Food Chemistry 342 (2021) 128347.

In-Situ Arsenic(III) Colorimetric Detection Exploiting Hydride Generation and Metal Organic Framework Ag-BTC Integrated in a 3D-Printed Millifluidic Device

PSC-16

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Keywords: *Arsenic, Hydride generation, Metal-organic framework, RGB readout, 3D printed*

Arsenic is an element with high toxicity, which causes concern due to its environmental presence [1]. Arsenic occurs as As(III) (arsenite) and As(V) (arsenate), of which arsenite is the most toxic to humans and the most difficult to remove from bodies of water. In 2020, a study found that over 220 million people in more than 70 countries are likely affected by arsenic poisoning in drinking water [2]. In this context, the development of simple, portable and low-cost methods, that allow rapid determination of the presence of As-(III) in water is of great importance. In this work, the application of green chemistry principles exploiting advanced materials together with 3D printing technology [3], has allowed the design of a miniaturized device that required only 1 mL of sample for the on-site determination of As-(III) by hydride generation, reaching several advantages such as the low cost, easy operation and portable method, the minimization of reagent and sample volumes, and the consequent minimum generation of residues.

The in-situ determination of As-(III) is based on the hydride generation technique, for which the As-(III) present in the sample was reacted with 6 % (v/v) HCl and 1.5 % $NaBH_4$ reducing agent, producing arsine (AsH_3), a volatile hydride, which upon contact with an Ag-BTC metal organic framework (MOF) sensor supported on a 3D printed device, generates silver (Ag) nanoparticles, allowing the color change. High resolution of 3D printed has made it possible to manufacture a miniaturized device designed in single piece (**Figure 1**), which consists of 3 important parts: an injector for the sample and reduced agent (which has a 1.5 mm in diameter channel, therefore, it is classified as a millifluidic device) [4]; a well for hydride generation (which has a network of zigzag-shaped channels that prevent the flow of microdroplets generated during the reaction); and the detection zone, which consists of a 3D printed piece in the form of lid (internally coated with the Ag-BTC MOF) that allows the microfluidic device to be hermetically sealed, thereby ensuring the reproducibility of the detection method.

Colorimetric detection due to changing color of MOF Ag-BTC from white to dark brown as a function of As-(III) concentration, allows qualitative (visual) and quantitative determination by RGB readout colorimetry using a portable photographic light box and a smartphone to capture the images. Additionally, a code has been developed in Image J to fast processing of these images.

This method does not have significant interference with other elements that generate volatile hydrides such as Hg, Sn and Se, and, under optimal condition, a linear range from 50 to 500 µg L^{-1} has been achieved for arsenic-(III) in water samples.

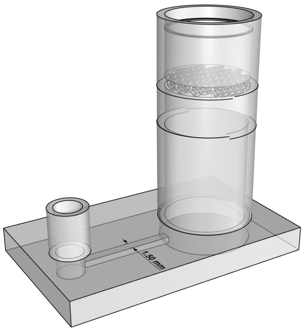

Figure 1. Millifluidic device to arsenic-(III) determination by hydride generation and colorimetric detection.

Acknowledgements
The authors acknowledge financial support from project PID2019-107604RB-I00 MICIU/AEI/10.13039/501100011033. L. Maza acknowledges a scholarship from Fundación Carolina. M.A.V-M. acknowledges the support from the Spanish Ministerio de Educación y Ciencia for the pre/post-doctoral research fellowship (FPU19/06082).

References

[1] F. Zhuang, J. Huang, H. Li, X. Peng, L. Xia, L. Zhou, T. Zhang, Z. Liu, Q. He, F. Luo, H. Yin, D. Meng, Biogeochemical behavior and pollution control of arsenic in mining areas: A review, Front Microbiol. 14 (2023) 1043024.
[2] J. Podgorski, M. Berg, Global threat of arsenic in groundwater, Science 368 (2020) 6493.
[3] World Health Organization, Arsenic mitigation for safe groundwater: report by the Secretariat, Executive Board. 118 (2006).
[4] P.J. Kitson, M.H. Rosnes, V. Sans, V. Dragone, L. Cronin, Configurable 3D-Printed millifluidic and microfluidic 'lab on a chip' reactionware devices, Lab Chip. 12(18) (2012) 3267.

Lab-On-Paper Colorimetric Device for Extraction-Free Phenolic Fraction Evaluation in Olive Oil

PSC-17

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Keywords: *In-field analysis, Gold nanoparticles, Silver nanoparticles, Office-grade technologies, Smartphone-based*

In balanced diets and nutraceutical foods, the antioxidants exert a preventive and benefic role for human health, indeed the European Food Safety Authority defined the phenolic compounds (PCs) as functional molecules, recommending their daily intake [1,2]; for these reasons, PCs can be considered food quality markers. In this context, extra-virgin olive oil (EVOO) is a highly valued product because rich in unsaturated fatty acid and phenolic compounds (PCs). However, the one-shot analysis of total phenols content (TPC) and their antioxidant capacity (AOC) in EVOO is still an open challenge due to the need for time and solvent-spending extraction procedures before analysis [1].

Herein is presented a disposable and portable colorimetric lab-on-paper device able to simultaneously determine the TPC and AOC of the EVOO polyphenols, without the need for extraction. The proposed device was designed using free software and fabricated with office-grade substrates (chromatographic paper, thermoplastic, and polymeric sheets). The device modules' geometries were realized with a craft-cutter machine, while the device assembling and colorimetric nanoprobes formation was achieved by thermal lamination. The proposed colorimetric lab-on-paper is pocket-sized and is a total analysis system since encloses all the steps for the direct EVOO phenolic compounds evaluation as sampling, analyte extraction, chemical reactions, and colorimetric detection (Figure A).

The colorimetric assay occurs in 15 minutes and relies on three steps: (i) sample loading, (ii) analytes transport to the readout zones, where the colorimetric nanoprobes (silver/Ag and gold/Au nanoparticles) are hosted, and (iii) double colorimetric analysis exploiting the AgNPs and AuNPs growth mediated by EVOO PCs which results in a color increase (iii). The color evolution is visually appreciable; thus, the colorimetric signal was easily acquired through a smartphone camera (iii). Noteworthy, the Au and Ag nanoprobes reactivity coupled to the lab-on-paper configuration allows the contemporary evaluation of TPC and AOC (Figure B). The Au and Ag-based colorimetric assays were calibrated employing hydroxytyrosol as reference standard, achieving good linearity ($R^2 \geq 0.998$) and useful LODs (≤ 6 mg L^{-1}). The developed pocket device allowed the direct analysis of 30 EVOO samples from different cultivars (Figure B), the data obtained resulted well correlate with conventional spectrophotometric methods ($r > 0.92$) for TPC (Folin-Ciocalteu) and AOC (ABTS) evaluation.

The lab-on-paper result cost-effective (0.03 € per device) and exploitable out of labs thanks to the pocket-size configuration and solvent-free analysis. The here proposed device is a valid prototype for a new generation of 'pop' and customizable sensors integrating nanomaterials.

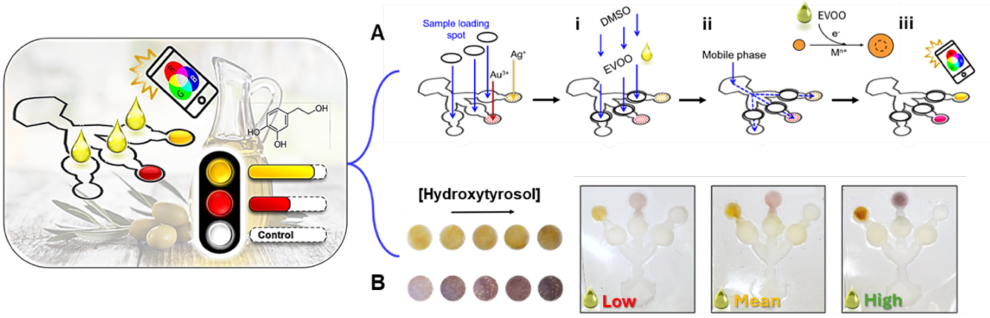

Figure. (**A**) Lab-on-paper set-up and colorimetric assay steps. (**B**) Pictures of the dose-response curve obtained with increasing concentrations of hydroxytyrosol and three devices used to evaluate EVOO samples with increasing polyphenol content.

Acknowledgments
This research was funded by the European Union – Next Generation EU. Project Code: ECS00000041; Project CUP: C43C22000380007; Project Title: Innovation, digitalization and sustainability for the diffused economy in Central Italy – VITALITY

References

[1] A. Della Pelle, F. Della Pelle, M. Del Carlo, D. Compagnone, Optical plasmonic sensing based on nanomaterials integrated in solid supports. A critical review. Analytica Chimica Acta 1237 (2023) 340594.

[2] A. Scroccarello, F. Della Pelle, D. Rojas, G. Ferraro, E. Fratini, S. Gaggiotti, A. Cichelli, D. Compagnone, Metal nanoparticles based lab-on-paper for phenolic compounds evaluation with no sample pretreatment. Application to extra virgin olive oil samples. Analytica Chimica Acta. 1183 (2021) 338971.

Europium-Based Luminescent Metal-Organic Framework (Eu-MOF) Immobilized on a 3D-Printed Device as a Multisample Fluorescent Sensor for In-Situ Smartphone-Assisted-Detection of Tetracyclines in Water Samples

PSC-18

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Keywords: *Eu-based metal-organic framework, Fluorescence sensor, Smartphone-assisted detection, Tetracyclines, 3D-printed portable device*

Tetracyclines (TCs) are a class of antibiotics widely used for the treatment of animal and human infections. However, inappropriate use of TCs can cause antibiotic resistance and lead to adverse effects on human health and the environment. Therefore, a rapid, selective, sensitive and on-site analysis is of great interest in research to guarantee food safety and estimate environmental contamination [1,2].

In this work, a novel fluorescent sensor has been developed for visually and rapidly detect TCs in water samples. Herein, a europium-based metal-organic framework (Eu-MOF) was synthesized using a facile and green method, and then immobilized on the wells of a 3D-printed microplate by mixing the lanthanide MOF with the polymer polyvinylidene difluoride (PVDF). Optimization of the mixing ratios (Eu-MOF/polymer) resulted in a hydrophobic coating with a high fluorescence emission, enabling multisample analysis with good selectivity and notable device recyclability. The proposed Eu-MOF sensor showed a strong and stable red fluorescence emission when was excited at 310 nm, and fluorescence quenching (emission at 615 nm) was immediately observed upon contact with TCs.

For detection, a portable 3D-printed platform, using a UV lamp as a radiation source and a smartphone for image capture, was built. The captured images were analyzed using ImageJ software to determine RGB color intensities.

Under optimized conditions, the proposed fluorescent sensor shows promise for reliable and real-time detection of TCs in numerous aqueous samples. The initial results, without preconcentration, allow the detection of TC concentrations between 20 and 500 μM, with a detection limit of 10 μM. For a more sensitive and selective detection, it is intended to pre-concentrate the analytes with a solid phase extraction cartridge.

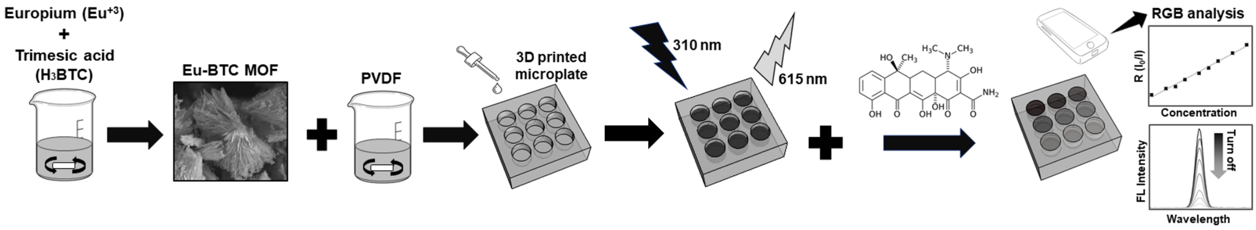

Figure 1. Illustration of the synthesis and immobilization processes of the Eu-MOF, as well as the application of the resulting fluorescent sensor device for detecting TCs.

Acknowledgements
The authors acknowledge financial support from project PID2019-107604RB-I00 MICIU/AEI/10.13039/501100011033. M.A.V-M. acknowledges the support from the Spanish Ministerio de Educación y Ciencia for the pre/post-doctoral research fellowship (FPU19/06082).

References

[1] F. Ahmadijokani, Hossein Molavi, S. Tajahmadi, M. Rezakazemi, M. Amini, M. Kamkar, O. J. Rojas, M. Arjmand, Coordination chemistry of metal–organic frameworks: Detection, adsorption, and photodegradation of tetracycline antibiotics and beyond, Coord. Chem. Rev. 464 (2022) 214562.
[2] Z. Zhang, Y. Zhang, H. Jayan, S. Gao, R. Zhou, N. Yosri, X. Zou, Z. Guo, Recent and emerging trends of metal-organic frameworks (MOFs)-based sensors for detecting food contaminants: A critical and comprehensive review, Food Chem. 448 (2024) 139051.

Electrochemical Sensor Manufactured on Algae-Paper Equipped with Nanobiochar from By-products for Bisphenol-A Determination in Zebrafish Embryo Model

PSC-19

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Keywords: *Paper-based sensors, Electrochemical sensors, In-vivo environmental model, Bisphenol-A exposure, biochar*

Bisphenol A (BPA) has become a widespread contaminant, commonly found in the environmental waters due to human activities, that can affect, directly or indirectly, aquatic ecosystems and human health. Herein, paper derived from recycled seaweed biomass (Algae paper) has been employed for the first time for the manufacturing of lab-made electrochemical sensors, that were employed for BPA monitoring in zebrafish embryos (Z-EBs; *Danio rerio*) and their culture medium used as an in-vivo and environmental model, respectively.

At first, the capability of Algae paper to support the stencil printing process employed for the sensor fabrication was evaluated employing different kinds of graphitic conductive inks; data obtained were compared with electrodes fabricated on other papers (kraft and office papers) and polyethylene terephthalate (PET). Algae paper sensors returned performances superior to office and kraft papers, and even PET. To improve the paper-sensors performance, two different kinds of biochars (BH), with amorphous (A) and nanofibrillar (F) structures, were tested; both BH, produced from industrial by-products, were nanodispersed in water-phase through a sonochemical method, avoiding the use of organic solvents [1,2].

The most performing Algae paper sensor was employed to monitor BPA levels during an eco-toxicological study conducted with Z-EBs exposed to different BPA levels (**Figure 1**). The sensor was able to directly determine BPA within Z-EB culture medium, showing robust analytical performance without matrix effect, allowing BPA quantification (LOD = 48 nM) in a useful linear range (0.25 - 6 μM), returning quantitative recoveries (95-113%). Afterward, the BPA bioaccumulation in Z-EBs during ecotoxicological studies was determined using the Algae-paper sensor; despite the inherent complexity of embryos, in matrix calibrations returned useful linearity (0.25 – 8 μM) and a LOD of 57 nM, allowing the estimation of the BPA bioaccumulated within Z-EBs (recoveries: 98-114%; RSD≤5.4%, n=3).

Summing up, the marriage between Algae-paper and BH gave rise to an effective analytical tool for monitoring BPA in Z-EBs, employed as an environmental (culture medium) and toxicological (embryos) model. This study proves how by-products can become active and functional parts of analytical devices, creating a virtuous circle able to offer sustainable solutions for environmental monitoring.

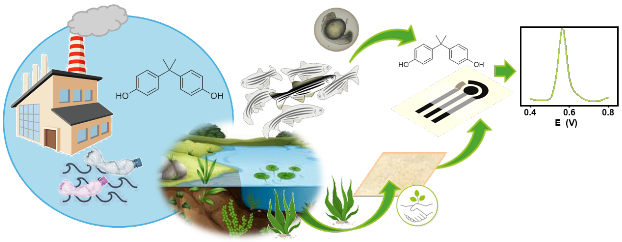

Figure 1. Algae-paper sensor circularity.

Acknowledgements
This research was funded by the European Union – Next Generation EU. Project Code: ECS00000041; Project CUP: C43C22000380007; Project Title: Innovation, digitalization and sustainability for the diffused economy in Central Italy - VITALITY

References

[1] S. Fiori, F. Della Pelle, F. Silveri, A. Scroccarello, E. Cozzoni, M, Del Carlo, D. Compagnone. Chemosphere 317 (2024) 137884.
[2] Q.U.A. Bukhari, F. Silveri, F. Della Pelle, A. Scroccarello, D. Zappi, E. Cozzoni, D. Compagnone. ACS Sustainable Chemistry & Engineering 9 (2024) 13988-13998.

Automated Preparation of Multi Compound Calibration Standards according to SANTE Requirements

PSC-20

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Keywords: *Automation, Calibration, Dilution, Preparation of mixed standards, SANTE criteria*

The preparation of multi-pesticide working standards for calibration is a recurring, highly critical and labor-intensive task for every analytical laboratory. The manual liquid handling steps are often error prone and subject to individual variation. It is reported from a recent survey that up to 50% of errors in chemical analysis are related to sample handling and human bias. Automation of the liquid handling processes significantly reduce the occurrence of errors, the consumption of solvents and consumables for sustainable and green analytical laboratory methods. Repeated processing on errors is avoided and the data quality and reproducibility improved.

For pesticide analysis, where a large number of calibration compounds need to be consolidated, the requirements for preparation and documentation are regulated in the SANTE document 11312/2021 in section F “Pesticide standards, stock solutions and calibration standard solutions” implemented by 01/01/2024 [1, 2].

For the preparation of multi-pesticide calibration standards the SANTE analytical quality control and method validation document sets this major requirements:

- Reference standards of analytes should be of known purity and must be assigned with a unique identification code.
- Standard vials should be permanently labelled.
- The standard preparation should be fully traceability including the source of supply, badge number, date of receipt and place of storage.
- Reference substances and stock solutions should be stored at low temperature, preferably in a freezer, with light and moisture excluded.
- Handling of the supplier’s expiry date.
- The date of preparation, the identity and mass (or volume, for highly volatile analytes) of the reference standard, and the identity and volume of solvents (or other diluents) must be recorded.
- Standards should be remixed after equilibration to room temperature.
- The “reference” standard should be weighed using a 5 decimal place balance.
- Volatile liquid analytes should be dispensed by volume or weight (if the density is known) directly into solvent.
- If septa are punctured they should be replaced as soon as possible.
- The documentation should ensure full traceability of all steps.

The poster describes the configuration and workflow for the automated preparation of standard mixes. The presented “CHRONECT MultiMix” workstation is based on a modular x,y,z-robotic system with two independently moving heads working simultaneously. The functions and tasks of each of the installed tools and modules are described.

A comprehensive User Interface including the data management software with a database of > 600 pesticides is provided for the definition and automated preparation of working standards. The export of the defined compound and concentration tables to data and LIMS systems is included.

Reference materials as well as the prepared working standards and calibration dilutions are stored dark in a Peltier-cooled drawer, which is permanently flushed with dry inert gas. Traceability is ensured through the use of 2D-barcodes on all vials. Vial barcodes are checked and registered before every liquid handling step. Racks for temporary room temperature equilibration and a vortex mixer for different vial sizes are provided. Punching of septa is avoided by using a decapper/recapping station. A 5-digit balance enables precise gravimetric monitoring of potential solvent evaporation. Multi-compound stock solutions from reference materials as well as the dilutions for daily calibrations can be prepared automatically and unattended by the MultiMix Workstation. The automated workflow provides highly reproducible, accurate and well documented standard preparations and dilutions. The automation leads to a significant reduction in consumables, reduces solvent use and works unattendedly. The dilution workstation fulfils the SANTE criteria according to 11312/2021. The described Multimix Workstation setup and workflow can also be applied to other analyte groups beyond pesticides.

References

[1] Directorate-General for Health and Food Safety. 2024 “Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis SANTE 11312/2021 v2”. Available at: https://food.ec.europa.eu/system/files/2023-11/pesticides_mrl_guidelines_wrkdoc_2021-11312.pdf

[2] Directorate-General for Health and Food Safety. 2023. “Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-Approval Control and Monitoring Purposes SANTE/2020/12830.” Sante/2020/12830, February 14: 1–50. Available at: https://food.ec.europa.eu/system/files/2021-03/pesticides_ppp_app-proc_guide_res_mrl-guidelines-2020-12830.pdf

Whey Proteins as a Source of Essential Minerals Evaluation of More Environmentally Friendly Analytical Methods

PSC-21

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Keywords: *Experimental design, Multielemental analysis, Sample preparation, TXRF, Whey proteins*

About 20 % of the total protein content of milk consists of whey proteins. Whey proteins are widely used in the food industry due to their nutritional value and their remarkable physico-chemical and functional properties. It is a highly nutritious substance that contains a variety of necessary components that support overall health and improve general well-being. Whey protein usually contains important minerals such as calcium, phosphorus, magnesium, potassium, zinc etc. These minerals have important functions in various physiological processes in the body. By including whey protein in your diet, you can get a significant amount of essential minerals that improve overall health and well-being, while benefiting from a useful source of high-quality protein [1]. However, the mineral composition can vary depending on factors such as processing methods and protein source.

Given the various functions of whey proteins, it is important to gather data on their elemental composition, as this can influence the quality, efficacy and safety of the product. This study describes the development of a suspension method for elemental determination by total reflection X-ray fluorescence spectrometry (TXRF) [2] in whey protein samples as a simple and environmentally friendly approach using response surface methodology (RSM). A Box-Behnken design was used to find optimal conditions for the method through a response surface study [3]. Three variables were considered in the optimization study: sample amount, dispersant and sample deposition volume.

The whey protein sample used in the optimization study was first analyzed by inductively coupled plasma mass spectrometry (ICP-MS) after microwave digestion in a closed vessel and the elemental composition was calculated. In order to determine the best conditions for preparing sample suspensions to analyse all analytes, we compared the results obtained using the TXRF method with those obtained using the established microwave digestion method in a closed vessel and analyzed by ICP-MS for recovery studies.

References

[1] M. Blažić, S. Zavadlav, E. Kralj, G. Šarić, Production of whey protein as nutritional valuable foods, Croat. J. Food Sci. Technol. 10 (2018) 255-260.
[2] R. Dalipi, E. Marguí, L.Borgese, L.E. Depero, Multi-element analysis of vegetal foodstuff by means of low power total reflection X-ray fluorescence (TXRF) spectrometry, Food Chem. 218 (2017) 348-355.
[3] M. Khajeh, Optimization of microwave-assisted extraction procedure for zinc and copper determination in food samples by Box-Behnken design, J. Food Compos. Anal. 22 (2009) 343-346.

Catalysis of [3+2] Cycloadditions by Acetic Acid Using Microwaves or Ultrasound

PSC-22

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Keywords: *Cycloaddition, Microwaves, Ultrasound*

The [3+2] dipolar cycloaddition is one of the most used reactions in organic synthesis, used to construct five-membered rings. The concept is based on the interaction of a 1,3-dipole molecule (a three-atom entity) and a dipolarophile (a two-atom entity). Dipoles, as the key structures in the reaction, are fragments consisting of three linked atoms usually C, O, N, and S. This system has to include four delocalized π electrons whose role is to form charge centers by suitable distribution. On the other hand, dipolarophiles can be any double or triple-bonded species. Most of [3+2] cycloadditions proceed through a concerted reaction mechanism resulting in high regio- and stereoselectivity.

Our group is interested in [3+2] cycloadditions of the enone systems. We reported the dipolar cycloaddition between vinyl enones and *N,N'*-cyclic azomethine imines as a convenient way to bicyclic dinitrogen-fused cores [1]. The usual experimental procedure exploited catalysis by acids. In continuation of our research, acetic acid as a benign solvent and catalyst were tested. In this report, we will present the data collected by examination of the reactions between vinyl enones and azomethine imines in the presence of acetic acid as a catalyst. The reactions were performed in a microwave reactor and ultrasound bath which particularly shortened the reaction and enabled the usage of a minimal amount of environment-friendly catalyst such as acetic acid.

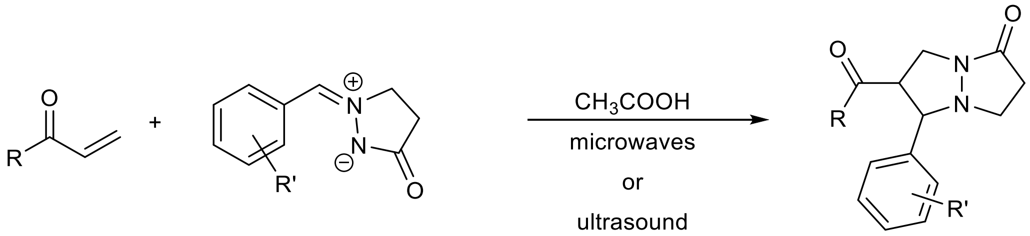

Figure 1. Dipolar cycloaddition of azomethine imines and vinyl enones.

Acknowledgements
The authors are grateful to the Ministry of Science, Technological Development and Innovation of the Republic of Serbia for financial support (Grant Nos. 451-03-65/2024-03/200122 and 451-03-66/2024-03/200122).

References

[1] J.P. Jovanovic, G.A. Bogdanovic, I. Damljanovic, Acid-Catalyzed [3+2] Cycloaddition of Enones with Azomethine Imines for Easy Access to Tetrahydropyrazolopyrazolones, Synlett 28 (2017) 664-668.

Audio-Tactile Pictures for Teaching Spectrometry to Individuals with Visual Impairments Towards Accessibility

PSC-23

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Keywords: *Audio-tactile images, Education, Inclusion, Spectrometry, Visual impairments*

Despite the significant effort that is being made towards the employment of novel educational approaches in chemistry teaching, the inclusion of people with visual impairments is still neglected. This results in significant challenges for these students during their studies, especially regarding the hands-on work in a laboratory which is a significant part of their educational journey. Audio-tactile pictures have been recently proposed for teaching the main chromatographic techniques to individuals with visual impairments [1]. This approach is based on a novel technology that utilizes a specific touchpad device (IVEO) and tactile images, printed on microcapsule paper. These images are placed on the touchpad, and verbal descriptions are provided for educational purposes. In this case, the user with blindness touches the tactile images and at the same time receives by audio a large number of verbal descriptions. This multimodal approach assists in the perception and understanding of images and diagrams by people with blindness or visual impairments. In this work, audio-tactile pictures were used for teaching the main spectrometric techniques to individuals with blindness. These pictures corresponded to the configuration of the main spectrometric techniques used for organic and inorganic analytes determination including the configuration of an ultraviolet spectrometer, an ultraviolet spectrum, and the configuration of a flame atomic absorption spectrometer. The development of such images was performed to enhance the understanding of people with blindness for the spectrometric instruments and the results obtained through their use. These techniques are commonly found in the food industry, pharmaceutical industry, toxicological laboratories, environmental pollution laboratories, etc. Thus, it will assist in the familiarization of people with blindness to perform experiments with the equipment that is commonly found in chemistry laboratories, enhance their confidence in working with them, and encourage them to gain practical experience.

Acknowledgments

The project was funded by the Royal Society of Chemistry Inclusion and Diversity Fund ('RSC').

References

[1] V. Samanidou, N. Manousi, F. Raptopoulou, L. Isaraj, K. Papadopoulos, Can Chemistry Be Accessible For Students With Visual Impairment?, Column 19(11) (2023) 19-22.

Advancements in Electrolyte Modification for Enhanced Safety and Sustainability in Lithium-Ion Batteries

PSC-24

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Keywords: *Battery, Electrolyte, Sustainable lithium-ion battery technology*

Transitioning to a sustainable energy future necessitates the development of high-energy-density, safe, cost-effective, and environmentally benign energy storage solutions. Lithium-ion batteries (LIBs) currently dominate the global energy storage landscape; however, concerns persist regarding their safety, cost, and environmental impact, largely due to the flammable and toxic nature of conventional electrolytes [1]. Addressing these challenges requires a paradigm shift towards greener electrolyte formulations that minimize chemical hazard potential and reduce environmental risks throughout their life cycle.

This research focuses on improving the safety and sustainability of LIBs by enhancing the thermal stability of electrolytes. The inherent safety issues arising from exposure to mechanical, thermal, or electrical abuse stem from the use of highly volatile and flammable organic solvent-based electrolytes [2,3]. To mitigate these risks, we investigate the use of novel zwitterionic compounds as electrolyte additives, aiming to stabilize electrode materials while simultaneously enhancing safety and performance.

Physicochemical, thermal, and electrochemical testing is conducted to evaluate the stability and performance of electrolytes containing these newly synthesized compounds. Specifically, we examine electrolytes comprised of 1.0 M LiPF6 in an ethylene carbonate/dimethyl carbonate (EC/DMC = 50/50) solvent mixture, comparing them to commercially available counterparts. These results demonstrate promising improvements in electrolyte stability and electrochemical performance, highlighting the potential of green chemistry approaches to drive innovation in energy storage technology. By embracing the principles of green chemistry, this research endeavors to minimize chemical hazard potential and reduce environmental impact, paving the way toward safer, more sustainable lithium-ion battery technology.

Acknowledgments

The authors gratefully acknowledge the financial support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Grants No. 451-03-66/2024-03/200125 & 451-03-65/2024-03/200125). This research was supported by the Science Fund of the Republic of Serbia, #11036, The new ionic additives for safer and durable electrolytes in lithium-ion batteries – SafeLi.

References

[1] M. Armand, P. Axmann, D. Bresser, M. Copley, K. Edström, C. Ekberg, D. Guyomard, B. Lestriez, P. Novák, M. Petranikova, Lithium-ion batteries - Current state of the art and anticipated developments**,** J. Power Sources 479 (2020) 228708.

[2] G.G. Eshetu, J.-P. Bertrand, A. Lecocq, S. Grugeon, S. Laruelle, M. Armand, G. Marlair, Fire behavior of carbonates-based electrolytes used in Li-ion rechargeable batteries with a focus on the role of the LiPF6 and LiFSI salts, J. Power Sources 269 (2014) 804-811.

[3] Q. Wang, P. Ping, X. Zhao, G. Chu, J. Sun, C. Chen, Thermal runaway caused fire and explosion of lithium-ion battery, J. Power Sources 208 (2012) 210-224.

Natural Deep Eutectic Mixture as Environmentally Friendly Solvent for Pharmaceutically Active Ionic Liquid

PSC-25

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Keywords: *Deep eutectic mixture, Interactions, Ionic liquid, Solubility*

In recent years, a new class of ionic liquids (ILs) derived from active pharmaceutical ingredients (APIs) has been developed, offering low toxicity, engineered lipophilicity, and potential synergistic effects between their cations and anions, making them viable candidates for pharmaceutical applications. The ability to maintain APIs in a liquid state at room temperature addresses several challenges, such as polymorphism, simplifies industrial manufacturing, and enables direct topical administration. Improvements in API permeability through IL synthesis for transdermal or topical use are attributed to the low dissociation of API-based ILs resulting from ion pair formation. This ion pair formation, inherent to the ionic liquid structure, increases the lipophilicity of the drugs sufficiently to facilitate skin penetration and pharmacological action while reducing their capacity for systemic absorption. However, despite many room-temperature ILs being derived from local anesthetics and nonsteroidal anti-inflammatory drugs (NSAIDs), several combinations remain in a solid state with melting points below 100 degrees Celsius. Given their classification as ionic liquids and their potential to significantly enhance the physicochemical and pharmacological properties of APIs, identifying an appropriate solvent for their topical use is imperative. One innovative approach involves the use of natural deep eutectic solvents (NADESs), which are blends of two or more active pharmaceutical compounds, typically solid at room temperature. When combined in specific molar ratios, they form hydrogen bonds, experience significant depression in melting points, and remain in a liquid state at room temperature.

The presented research delves into the thermodynamic properties of a deep eutectic solvent created from natural molecules-menthol and lauric acid in a 2:1 molar ratio-and an ionic liquid based on two active pharmaceutical ingredients, benzocainium ibuprofenate. Initially, the limited solubility of benzocainium ibuprofenate in water was noted, prompting the preparation of a hydrophobic natural deep eutectic mixture of menthol and lauric acid in a 2:1 ratio to enhance the solubility of benzocainium ibuprofenate. To assess the solvent properties of DESs and ILs mixtures at different temperatures and their molecular interactions aimed at enhancing solvent performance, various parameters, including apparent molar volume, limiting apparent molar expansibility, and viscosity B coefficient, were estimated within a temperature range of T = 293.15 K to 313.15 K, considering varying concentrations of benzocainium ibuprofenate.

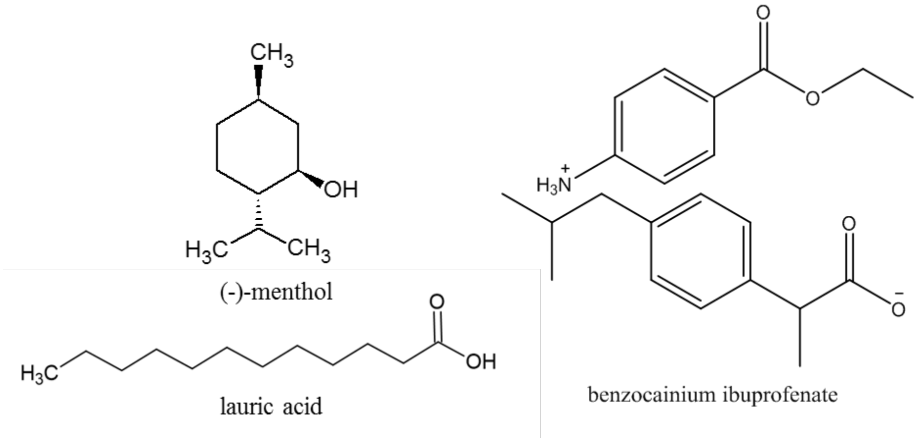

Figure 1. Chemical structures of the studied compounds.

Acknowledgments
The authors gratefully acknowledge the financial support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Grants No. 451-03-66/2024-03/200125 & 451-03-65/2024-03/200125) and the Secretariat for Higher Education and Scientific Research of the Autonomous Province of Vojvodina, Serbia (Grant No. 142-451-2545/2021-01/2).

SERS-Based Sandwich Immunoassay Platform for Non-Invasive Determination of IgG

PSC-26

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Keywords: *Human IgG, Immunoassay, Raman spectroscopy, SERS substrate, Ultrasonic-assisted fabrication*

Human immunoglobulin G (IgG) is one of the most common and abundant human serum proteins, which plays a crucial role in defense against viral and bacterial infections. Hence, detection of IgG in a timely manner is of critical importance for the early diagnosis of infectious diseases. The most representative method for analyzing the species and concentrations of IgGs is immunoassay, which is based on specific antigen-antibody interaction. Among the various detection techniques used for immunoassays, Surface-enhanced Raman spectroscopy (SERS) has gained increasing popularity in recent decades due to its unique advantages such as high sensitivity, minimal spectral overlap, and the ability to detect multiple components. SERS is a technique that significantly enhances the Raman signal when molecules are situated on a noble metal surface, such as silver or gold. Regarding SERS-based immunoassay, the initial requirement is the fabrication of a SERS-active substrate with high reproducibility, stability, and signal enhancement [1,2].

Herein, we propose the fabrication of highly stabile and reproducible SERS substrates for the determination of human IgG from saliva. The fabrication process involves the sintering of gold nanopowders (AuNPs) laid onto the PMMA substrate through the generation of heat by ultrasonic vibration. A 600 W ultrasonic welder with a stepped cylindrical horn vibrating at 30 kHz was employed. The initial stage of the process involved the cutting of a 2x2mm stencil on the protective film of PMMA. Following this step, chloroform was dripped onto the stencil to soften the PMMA substrate. AuNPs were then placed on the stencil and pressed on the substrate by the horn as the final step. Following a delay, the horn vibrated for 5 s. Subsequently, the horn was released after a cooling period, allowing for the removal of the substrate. The stencil was then peeled off the substrate and the gold layer was used as a SERS substrate.

Prior to the formation of the immunoassay, the fabricated SERS substrates were cleaned with ethanol. The self-assembled monolayer (SAM) was prepared by maintaining the SERS substrates in an 11-MUA solution in ethanol as the first step. The free carboxyl groups were then activated using an EDC/NHS based crosslinking mechanism. Then, the SERS substrates were interacted with anti-IgG antibody solutions and kept in a solution of BSA to block the unreacted activated esters and the free surface. In order to prepare DTNB-labelled anti-IgG conjugates, rod-shaped gold nanoparticles (AuNRs) were synthesized by using the seed-mediated growth technique [3]. The AuNRs were modified with 5,5′ -dithiobis(2-nitrobenzoic acid) (DTNB) as a Raman reporter. To conjugate DTNB labelled AuNRs with IgG antibodies, free carboxyl groups of DTNB molecules were activated by EDC/NHS based crosslinking mechanism. The free surfaces and unreacted activated groups were blocked with BSA. The formation of the sandwich complex was achieved by dropping varying concentrations of human IgG protein onto the SERS substrates and then interacted with DTNB-AuNR-IgG-Ab conjugate. Following the washing step, SERS analysis was performed.

The results demonstrated a linear relationship between the logarithms of IgG concentrations in the range of $5x10^{-6}$ to $5x10^{-1}$ mg/mL in a buffer solution. The corresponding SERS intensities to IgG concentrations exhibited a determination coefficient (R^2) value of 0.9819. Furthermore, the applicability of this methodology for the identification of analytes was performed using artificial saliva samples spiked with IgG.

Acknowledgements
The authors acknowledge The Scientific and Technological Research Council of Turkey (TUBITAK) for the financial support through Project 121M427.

References

[1] Q. Qu, J. Wang, C. Zeng, M. Wang, W. Qiabc, Z. Hea, AuNP array coated substrate for sensitive and homogeneous SERS-immunoassay detection of human immunoglobulin G, RCS Adv. 11 (2021) 22744-22750.
[2] Z. Wang, S. Zong, L. Wu, D. Zhu, Y. Cui, SERS-Activated Platforms for Immunoassay: Probes, Encoding Methods, and Applications, Chem. Rev. 117 (2017) 7910-7963.
[3] B. Nikoobakht, M.A. El-Sayed, Preparation and growth mechanism of gold nanorods (NRs) using seed-mediated growth method, Chem. Mater. 15 (2003) 1957-1962.

Polydopamine-Coated Steel Wire: Thin Film Microextraction Methodology for Diazepam and Nordazepam Detection

PSC-27

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Keywords: *Diazepam, Forensic Toxicology, Gas Chromatography, Polydopamine, Thin Film Microextraction.*

Introduced in 1963, diazepam quickly became a top-selling drug for treating CNS disorders like anxiety, epilepsy, and alcohol withdrawal, but its potential for dependence and abuse has led to its involvement in numerous forensic cases, including suicide, drug-driving, and robbery [1].

The detection and quantification of diazepam in complex matrices present significant challenges due to its low concentration and the presence of interfering substances. This study explores the development of a novel polydopamine-coated steel wire for thin film microextraction (TFME) aimed at improving the extraction efficiency and analytical performance for diazepam detection. The polydopamine coating was applied using an electropolymerization method. Cyclic voltammetry (CV) was carried out from −0.8 to +0.5 V at a scan rate of 50 mV/s over 5 cycles to achieve a uniform and robust film. Known for its strong adhesive properties and biocompatibility, the polydopamine-coated steel wire created a highly selective and sensitive extraction medium. Key parameters influencing the extraction process, such as coating thickness, extraction time, and desorption conditions, were systematically optimized.

The extracted diazepam was then analyzed using gas chromatography-mass spectrometry (GC-MS), which provided high sensitivity and specificity. For the analysis of diazepam, the GC-MS instrumentation consisted of an Agilent 6890N Gas Chromatograph coupled with an Agilent 5973 Mass Spectrometer. The gas chromatograph utilized a Restek RTX-5MS column (30 m × 0.25 mm i.d., 0.25 µm film thickness) with helium (99.999% purity) as the carrier gas at a flow rate of 1.0 mL/min. The injection was performed in splitless mode with an injection volume of 1 µL and an injector temperature set to 280°C. The oven temperature program was initiated at 100°C (held for 1 minute), followed by a ramp of 20°C/min to 250°C (held for 5 minutes), and then a final ramp of 10°C/min to 300°C (held for 10 minutes). The mass spectrometer operated in electron impact (EI) ionization mode, with the ion source temperature set at 230°C, the quadrupole temperature at 150°C, and the transfer line temperature at 280°C. The mass range was set from 50 to 500 m/z, and the acquisition was carried out in selected ion monitoring (SIM) mode, specifically targeting diazepam and nordazepam.

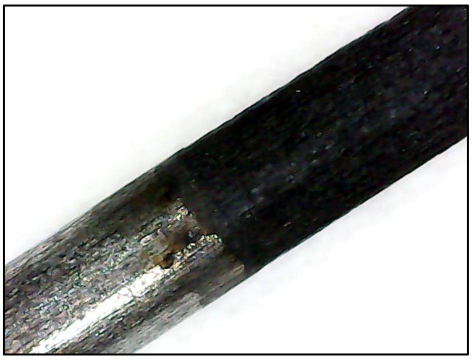

Figure 1. Polydopamine-coated (black part) steel wire prepared via electropolymerization for thin film microextraction of diazepam.

TFME offers several advantages, including reduced solvent consumption, minimal sample preparation, and enhanced sensitivity and selectivity [1]. The performance of the polydopamine-coated steel wire was evaluated using standard analytical techniques, demonstrating significant improvements in extraction efficiency, repeatability, and detection limits compared to traditional methods. This innovative approach offers a promising alternative for the rapid and accurate detection of diazepam in various biological and environmental samples, contributing to advancements in forensic and environmental toxicology.

References

[1] L.L Wang, X.X. Ren, Y. He, G.F. Cui, Z.W. Wei, J. Jia, J. Cao, Y. Liu, B. Cong, Y. Niu, K.M. Yun, Study on the pharmacokinetics of diazepam and its metabolites in blood of Chinese people. European Journal of Drug Metabolism and Pharmacokinetics, 45 (2020) 477-485.
[2] H. Musarurwa, Advances in thin film micro-extraction (TFME) of selected organic pollutants, and the evaluation of the sample preparation procedures using the AGREEprep green metric tool, Microchemical Journal (2024) 110938.

Vacuum-Assisted Headspace Solid-Phase Microextraction Analysis of Energy Drinks

PSC-28

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Keywords: *Gas chromatography Mass spectrometry, Stainless-steel valves, Vacuum-assisted headspace solid-phase microextraction*

The growing consumption of energy drinks every year is a major concern, when studies showing that adolescents and young people are the primary consumers [1]. Energy drinks can contain organic compounds such as benzoic acid, propanoic acid, benzaldehyde, citronellol and furfural, which pose health risks. Studies with determination of organic compounds in different matrices have highlighted the successful application of the solid phase microextraction (SPME) method, originally introduced by Janusz Pawliszyn [2]. Therefore, the application of accurate and highly sensitive methods for the determination of organic compounds based on solid phase microextraction in energy drinks is an important challenge. In this regard, the analysis was performed using the vacuum headspace solid-phase microextraction (Vac-HSSPME) method, which was initially proposed by Elefteria Psillakis [3], that attracting an increasing interest within the realms of environmental and food analysis [4, 5, 6].

In this study organic compounds have been detected in energy drinks such as “Dizzy energy”, “Red Bull”, “Gorilla”, “Forsage”, “Zet”, “Tamga”, “Flash Energy”, “Monster” and “Adrenaline” purchased from local market using a Vac-HSSPME coupled with gas chromatography-mass spectrometry (GC-MS). For the first time, in this research used new stainless-steel valves with magnetic properties (Vac-SPME Arrow closures from ExtraTECH) [7], which work with autosamplers and eliminate the need for additional magnetic caps. Also, in this study explored how key factors such as extraction temperature, extraction time, fiber coating, and air evacuation time affect the method's effectiveness for determination of organic compounds in energy drinks.

The results showed that the Vac-HSSPME method is effective and selective 3-4 times for extracting organic compounds from energy drinks compared with classical HSSPME. Overall, the automated Vac-HSSPME method with new stainless-steel valves demonstrated excellent performance in identifying and analysis organic compounds in energy drinks. Additionally, this study recommends following the Vac-HSSPME method coupled with GC-MS for precise and quantitative determination of organic compounds in energy drinks.

Acknowledgements

Authors thank financial support from the Ministry of Science and Higher Education of the Kazakhstan Republic of project program AP23490323, 2024-2026.

References

[1] H.A. Hamilton, A. Boak, G. Ilie, R.E. Mann, Energy drink consumption and associations with demographic characteristics, drug use and injury among adolescents, Canadian Journal of Public Health, 104 (2013).

[2] É.A Souza-Silva, J. Pawliszyn, Direct Immersion Solid-Phase Microextraction with Matrix-Compatible Fiber Coating for Multiresidue Pesticide Analysis of Grapes by Gas Chromatography-Time-of-Flight Mass Spectrometry (DI-SPME-GC-ToFMS). J. Agric. Food Chem. 63 (2015) 4464–4477.

[3] E. Psillakis, Vacuum-assisted headspace solid-phase microextraction: A tutorial review, Anal. Chim. Acta. 986 (2017) 12–24.

[4] Y. Syrgabek, M. Alimzhanova, S. Yegemova, S. Batyrbekova, Vacuum-assisted headspace-solid phase microextraction of pesticides in grape samples, Adv. Sample Prep. 11 (2024) 1–15.

[5] M. Mamedova, M.B. Alimzhanova, Determination of Biomarkers in Multifloral Honey by Vacuum-Assisted Headspace Solid-Phase Microextraction, Food Anal. Methods. 16 (2023) 1180–1190.

[6] M. Vakinti, S.M. Mela, E. Fern´andez, E. Psillakis, Room temperature and sensitive determination of haloanisoles in wine using vacuum-assisted headspace solid- phase microextraction, J. Chromatogr. A 1602 (2019) 142–149.

[7] https://extratech.gr/.

Molecularly Imprinted Polymer-Coated Toothpicks for the Determination of Diazepam and Major Metabolite

PSD-01

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Keywords: *Diazepam, Liquid Chromatography, Microextraction, Molecular imprinted polymers, Nordiazepam*

Green analytical chemistry (GAC) promotes the reduction of toxic chemicals/reactants usage, the use of energy-efficient equipment, and the generation of minimal waste. Because of the natural matrix of lignocellulosic materials, the principles of green analytical chemistry are applicable, enabling the design of sustainable devices [1]. Diazepam, a benzodiazepine medication, is prescribed for the treatment of alcohol withdrawal symptoms, including anxiety, agitation, and tremors [2]. As diazepam carries a risk of addiction and dependency, it is essential to ensure effective monitoring of treatment efficacy and adherence.

This study focuses on developing a highly selective and sensitive molecularly imprinted polymer (MIP) coating on toothpicks for diazepam and nordiazepam detection (**Figure 1**). P-DOPA is obtained by dopamine auto-oxidation. Before applying MIP coating, the toothpicks were subjected to washing steps to eliminate potential interferences from the toothpick matrix. At this stage, the toothpicks were washed with water and dried in an oven at 37°C. The coating time was optimized, resulting in a homogeneous and uninterrupted appearance achieved through overnight coating. The removal efficiency of the template is evaluated using various types of organic solvents and acidic conditions.

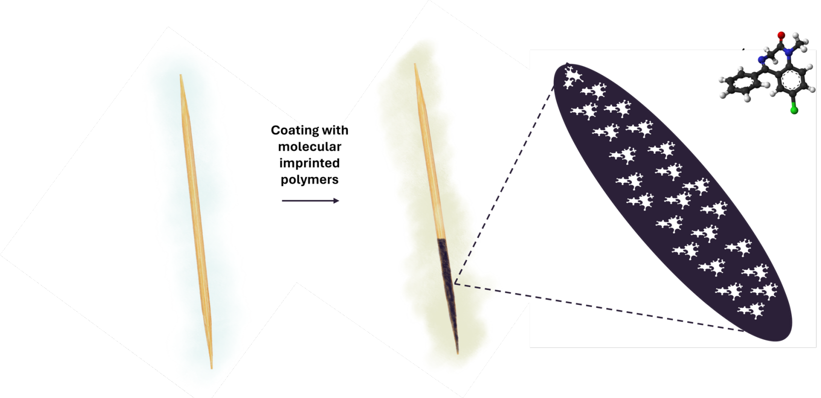

Figure 1. Formation MIP-layer on the toothpicks for the diazepam.

HPLC- UV was used for the optimization of the extraction conditions. Chromatographic separation was performed utilizing a Kinetex F5 analytical column (150 mm × 4.6 mm i.d., 5 μm) to determinate targeted compound. The isocratic mobile phase system was composed of a mixture of phosphate buffer (15 mM, pH 4.3) and acetonitrile 70:30, v/v at a flow rate of 1 mL/min. Detection was performed at a wavelength of 238 nm, with each sample injected. This highly selective extraction and analysis method offers a promising approach for detecting diazepam, customizing treatment, and enhancing its efficacy.

References

[1] J. Millan-Santiago, R. Lucena, S. Cardenas, Wooden-based materials: Eco-friendly materials for direct mass spectrometric analysis and microextraction, J Sep. Sci. 45 (2022) 223-232.

[2] R.S.H. Ron M. Walls, Marianne Gausche-Hill, Katherine Bakes, Jill Marjorie Baren, Timothy B. Erickson, Andy S. Jagoda, Amy H. Kaji, Michael VanRooyen, Richard D. Zane, Rosen's Emergency Medicine: Concepts and Clinical Practice, Ninth Edition, Elsevier, Philadelphia, PA2018.

Supported Liquid Extraction Using Wetted Nanofibrous Discs as a Simple Approach for In Vial Extraction Prior to Chromatography Analysis

PSD-02

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Keywords: *Chromatography, Nanofibrous discs, Octanol, Polymer nanofibers, Supported liquid extraction (SLE)*

Due to high porosity, large surface area, and cost-effective manufacturing process, Polymer Nanofibers gained a lot of interest as sorbents for extracting trace-level contaminants [1]. They can undergo surface functionalization or be combined with other materials gaining better selectivity and stability [2]. Here, we propose a simple enhancement to the extraction capacity of nanofibrous discs. It involves wetting discs with a small volume of octanol right before the extraction. This novel Supported Liquid Extraction was tested to extract 9 common water contaminants with wide range of log P values (1.9 – 6.5). Three different nanofibrous polymers (polyacrylonitrile (PAN), polyhydroxybutyrate (PHB), and polylactic acid (PLA)) were chosen as sorbents. Nanofiber mats were fabricated by the alternating current electrospinning technique and cut into small discs. Extraction experiments were conducted in a beaker, with nanofiber discs attached to a metal wire as a home-made spinning device. After the extraction, desorption was performed in one-step, directly in HPLC vial. This approach limits manual operations, thus reducing human error. The addition of octanol showed a 20-fold increase of enrichment factor when compared to non-wetted discs. The developed method was applied to river water samples and showed good recovery (58.9 – 121.4 %), repeatability (RSD<13%), and linearity in a range 20-200 mg L^{-1}.

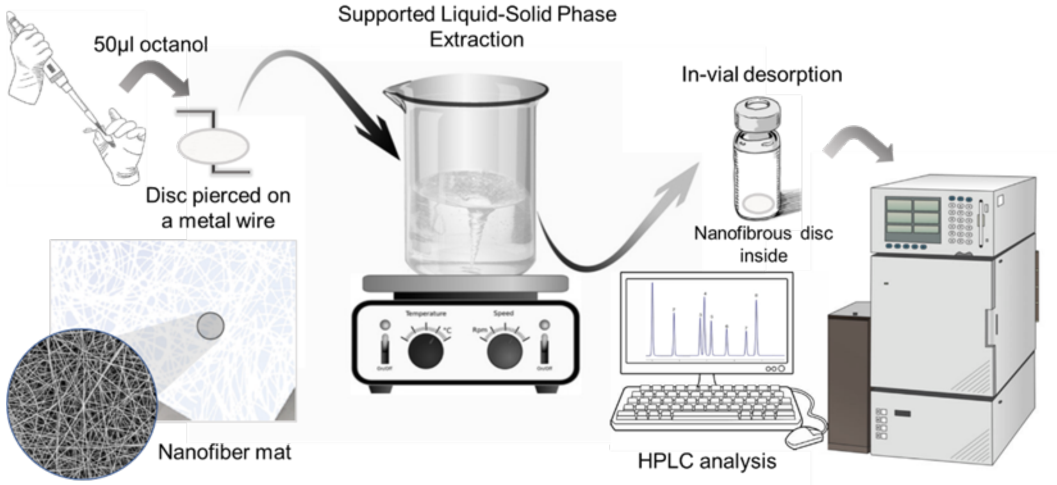

Figure 1. Schematic representation of the extraction procedure.

Acknowledgements
This work was supported by the Czech Science Foundation through the project no. 23-05586S and Charles University project GAUK no. 140/50/245001 and SVV 260 662.

References

[1] M. Háková, I. Chocholoušová Havlíková, P. Solich, F. Švec, D. Šatínský, Electrospun nanofiber polymers as extraction phases in analytical chemistry – The advances of the last decade, TrAC, 110 (2019) 81-96.
[2] E. Torabi, M. Moghadasi, M. Mirzaei, A. Amiri, Nanofiber-based sorbents: Current status and applications in extraction methods, J. Chromatogr. A 1689 (2023).

Upcycling Plastic Wastes as Supports for Preparation of Metal-Organic Framework-Based Sorbents

PSD-03

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Keywords: *Antibiotics, HDPE plastics, MOFs, Plastic waste, Sorbent*

Metal-organic frameworks (MOFs) are crystalline nano-porous materials with particular properties such as uniform and tunable pore size, high thermal stability, large surface areas and adsorption capacity, which make them suitable sorbent materials for sample preparation [1,2]. Despite their benefits, there is a growing demand for more convenient preparative routes that reduce costs, minimize environmental impacts, and allow the use of recyclable or renewable supports, aligning with the principles of the circular economy. For example, a recent trend involves the alternative preparation of MOFs from plastic waste, particularly polyethylene terephthalate, as a source of organic linkers, constituting a promising practice for the sustainable and low-cost production of high-value materials as MOFs and MOF composites [3,4]. However, other waste plastics made from organic polymer chains, such as polyethylene, polypropylene, and polyvinyl chloride, among others, have been little explored for recycling as sources or substrates for the preparation of MOFs.

Herein, the present work aims to use high-density polyethylene (HDPE) waste material as a substrate for the preparation of UiO-66, which will be used for extracting cephalosporins (CEFs) as model antibiotics. For this purpose, HDPE plastics were collected from research laboratory wastes and properly cleaned before use. Then, a chemical modification with several etchant reagents (nitric acid, hydrochloric acid, etc.) was performed to create reactive hydroxyl groups on the HDPE surface. Infrared studies were used to analyze and compare the changes that each reagent makes on the HPDE surface. The treated surfaces (with the highest hydroxyl content) were subsequently carboxymethylated and then used as scaffold for in-situ synthesis of UiO-66 to produce efficient and low-cost extraction units. The prepared MOF@HDPE support was characterized in depth by different techniques (infrared, microscopy, etc.). Besides, the extraction protocol was optimized (involving parameters such as loading/desorption times, eluents, etc.) along with the evaluation of performance features. Finally, the optimized analytical sample treatment procedure, combined with HPLC with diode-array detection, was successfully applied to the determination of low levels of CEFs in environmental water and urine samples.

Acknowledgements

The authors acknowledge financial support from the Spanish State Research Agency (AEI//10.13039/501100011033/), the Spanish Ministry of Science, Innovation and Universities (MICIU) and the European Union (NextGenerationEU/PRTR) through projects PID2021-125459OB-I00. Also, the authors acknowledge the projects CIGE/2023/069 and CIAICO/2022/183 funded by Generalitat Valenciana. The authors extend their appreciation to MICINN for granting the Spanish Network of Excellence in Sample preparation (RED2022-134079-T). This communication is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society.

References

[1] M. Bazargan, F. Ghaemi, A. Amiri, M. Mirzaei, Metal–organic framework-based sorbents in analytical sample preparation, Coord. Chem. Rev. 221 (445) 2021 214107.
[2] H. Martínez-Pérez-Cejuela, E.J. Carrasco-Correa, A. Moga, M. Vergara-Barberán, M. Beneito-Cambra, M.J. Lerma-García, E.F. Simó-Alfonso, J.M. Herrero-Martínez, Reticular framework materials in miniaturized and emerging formats in analytical chemistry, J. Chromatogr. A 1673 (2022) 463092.
[3] E-S.M. El-Sayed, D. Yuan, Waste to MOFs: sustainable linker, metal, and solvent sources for value-added MOF synthesis and applications, Green Chem. 22 (2020) 4082.
[4] T.F. Mastropietro, Metal-organic frameworks and plastic: an emerging synergic partnership, Sci. Tehcnol. Adv. Mat. 24 (2023) 2189890.

Core Shell Particles with Strong Cationic Exchange Moieties as Selective Material

PSD-04

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Keywords: *Contaminants, Core-shell particles, Environmental water samples, Ion-exchange interactions, Solid-phase extraction, Sorptive materials*

Core shell particles which are based on non-porous core surrounded with a porous shell offers a series of advantages when applied mainly as packing materials for chromatographic columns [1]. Nevertheless, in extraction techniques some approaches have been already presented in the preparation of core shell systems where the shell is a molecular imprinted polymer with different core materials such as silica, magnetic nanoparticles or quantum dots [2]. Except from this, form the best of our knowledge, polymeric core shell particles have been never prepared and applied in sorptive extraction techniques.

In the present study, a homemade polymeric sorbent has been developed through a two-step polymerization precipitation of divinylbenzene to obtain core microspheres. Then, the core microspheres were subjected to hypercrosslinking and sulfonation reactions to obtain the final sulfonated hypercrosslinked core shells. The new material, apart from the core shell morphology, can simultaneously present reversed-phase interactions (through the hypercrosslinked network in the shell) and cation-exchange interactions (through the sulfonated functional groups present in the shell) and act as an efficient mixed-mode ion-exchange sorbent [3].

For the first time, hypercrosslinked sulfonated core shells were applied for the solid phase extraction (SPE) of five basic pharmaceuticals from river, effluent wastewater and influent wastewater samples followed by liquid chromatography high resolute mass spectrometry (LC-HRMS).

The SPE parameters such as sample pH, washing and elution conditions were optimised to exploit these ionic interactions between compounds and the functional groups. When 100 mL of ultrapure water were loaded followed by the optimised SPE protocol, the core shell material provided recoveries higher than 70% for all the compounds, whereas similar recoveries were obtained when a non-core shell material [4] were used to upload 50 mL of ultrapure water, fact that highlight the importance in the particle morphology in the extraction.

The method using the core shell particles in SPE followed by LC-HRMS was also validated using river, effluent and influent wastewater samples with apparent recoveries between 44 and 108%, matrix effect ranging from -24 to +25 in all complex matrices, and limits of detection of the low ng/L.

Finally, the method was applied to the analysis of the studied environmental water samples and all five pharmaceuticals were found in all type of water with concentrations ranging <MDL to 320 ng/L in river, 65 to 6660 ng/L in effluent sewage and 139 to 8561 ng/L in influent sewage water samples.

Acknowledgements

These results are part of the project PID2020-114587GB-I00 and RED2022-134079-T funded by MCIN/AEI/10.13039/501100011033. A. Moral would also like to thank Universitat Rovira i Virgili (URV) for his PhD grant (2020PMF-PIPF-33).

References

[1] A. Ahmed, K. Skinley, S. Herodotou, H. Zhang, J. Sep. Sci. 41 (2018) 99–124.
[2] L. Wan, Z. Chen, C. Huang, X. Shen, Trends Anal. Chem. 95 (2017) 110–121.
[3] N. Fontanals, F. Borrull, R.M. Marcé, Anal. Chim. Acta. 1117 (2020) 89–107.
[4] N. Fontanals, N. Miralles, N. Abdullah, A. Davies, N. Gilart, P.A.G. Cormack, J. Chromatogr. A. 1343 (2014) 55–62.

A Novel Automatic Flow-Batch Liquid-Liquid Microextraction Lab-in-Syringe Platform Based on Natural Deep Eutectic Solvents for Toxic Metal Determination

PSD-05

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Keywords: *Automation, Lab-in-syringe, Liquid phase microextraction, Natural deep eutectic solvents, Toxic metals*

Automation in analytical chemistry has evolved tremendously over the past years, however, there is still a demand for designing fully automated flow setups. Currently, the combination of automatic systems with environmentally friendly microextraction/preconcentration methods has attracted the interest of researchers [1]. In this work, a novel fully automatic flow-batch liquid-liquid microextraction lab-in-syringe platform based on the use of natural deep eutectic solvents (NADES) has been proposed for toxic metal determination in water samples. NADES are a green alternative to conventional deep eutectic solvents which are formed from natural compounds, and they fully represent green chemistry principles. The analytical process of the developed included the in-syringe metal complexation, followed by the microextraction and preconcentration of the obtained complex using a natural deep eutectic solvent consisting of heptanoic acid: methol in a molar ratio of 2:1. The proposed platform was proposed as a front-end to flame atomic absorption spectrometry (FAAS) using Cd, Cu, and Pb as model analytes. The main attributes that can affect the performance of the novel system (i.e., NADES type and composition, complexing agent, sample pH, sample amount, and volume of NADES) were throughout studied. Under optimum conditions, the limits of detection were 0.54-4.52 µg L^{-1}, while the enhancement factors ranged between 31-55 for a sample consumption of 4000 µL. In all cases, the relative standard deviations were less than 3.8% demonstrating good method precision. Moreover, satisfactory method accuracy was obtained by analyzing standard reference materials. As a proof-of-concept, the novel system was used for the analysis of drinking and environmental water samples. The relative recoveries for Cd, Cu, and Pb ranged between 94.0-104.0%, showing good method applicability.

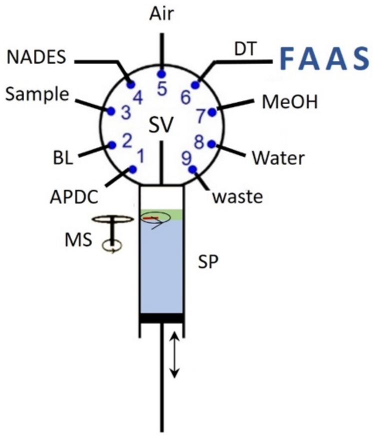

Figure 1. Schematic illustration of the automatic system for Pb, Cd, and Cu determination. SV: selection valve; DT: delivery tube; MS: magnetic stirrer; BL: blank solution.

References

[1] G. Giakisikli, A. Anthemidis, An automatic stirring-assisted liquid-liquid microextraction system based on lab-in-syringe platform for on-line atomic spectrometric determination of trace metals, Talanta 166 (2017) 364-368.

Evaluation of Metals Leachability from 3D Printed Analytical Devices

PSD-06

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Keywords: *Analytical devices, ICP-MS, Metal leaching, Three-dimensional (3D) printing*

Three-dimensional (3D) printing is a technique that is booming today and is present in a wide variety of applications in several areas. The most commonly used printing techniques, due to their affordability, ease of use, and low cost of materials, are fused deposition modeling (FDM) and stereolithography (SLA) [1]. In analytical chemistry, 3D printing has been employed in microfluidic devices, sensors, separation techniques, sample pretreatment, and sampling platforms [2,3]. Despite significant interest in these materials, an interference assessment based on the final device extracts has not yet been carried out, even though the printing process may potentially affect the quality of analytical results. For this reason, given the increase in the use of 3D printing in analytical chemistry, it is important to establish the metal leaching in different materials used for FDM and SLA printing, in order to avoid potential interferences.
Specifically, for the FDM technique, the most commonly used materials have been selected: polylactic acid (PLA), polypropylene (PP), and nylon (NY). For SLA, three materials of different hardness have been selected: Clear resin, with optical properties; an Elastic resin; and Rigid 10K resin, with high hardness and resistance.
These materials have been subjected to different concentrations of nitric acid to see how they are affected by long-term exposure. Subsequently, the leaching of these materials was analyzed for 30 heavy metals by ICP-MS. It has been observed that for the six selected materials, increasing the concentration of nitric acid significantly increases the concentration of leached metals (**Figure 1**). Furthermore, it has been noted that as the amount of acid increases, additional metals appear that did not appear at lower concentrations. Through the study of 3D printing materials, we aim to provide guidance on the potential metallic interferents.

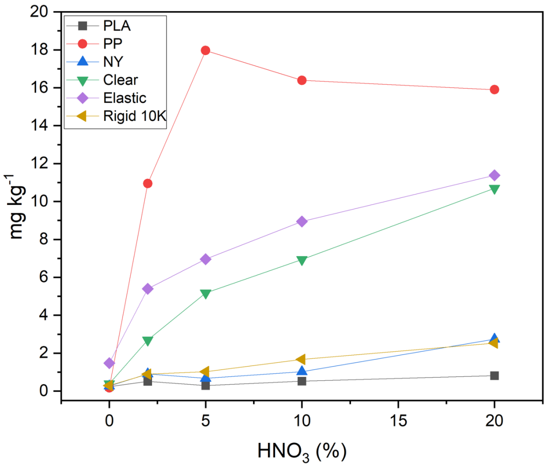

Figure 1. Total amount of metals leached by various materials at different acid concentrations.

Acknowledgements
Financial support from the Spanish Ministry of Science and Innovation, Agencia Estatal de Investigación (project PID2019-107604RB-I00/MCIN/AEI/ 10.13039/501100011033) is gratefully acknowledged.

References

[1] S.F. Iftekar, A. Aabid, A. Amir, M. Baig, Advancements and Limitations in 3D Printing Materials and Technologies: A Critical Review, Polymers 15 (2023) 2519.
[2] L. Wang, M. Pumera, Recent advances of 3D printing in analytical chemistry: Focus on microfluidic, separation, and extraction devices, TrAC Trends in Analytical Chemistry 135 (2021) 116151.
[3] M.A. Vargas-Muñoz, C. Palomino, G. Turnes, E. Palacio, 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, Journal of Environmental Chemical Engineering 11 (2023) 110503.

Polyvinyl Chloride Coated Paper Post-Modified with Diphenylamine: A Sustainable Sorptive Phase to Extract Opioids from Saliva Samples

PSD-07

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Keywords: *Cellulose, Direct infusion mass spectrometry, Opioids, Polyvinyl chloride, Thin-film microextraction*

The present work deepens the potential of cellulose paper in the preparation of planar sorptive phases that can be used under the thin film microextraction format. This substrate presents some advantages over classical commercial sorbents, including a sustainable character, potential biodegradable nature, and high porosity. Also, it can be modified easily to boost its interaction with the target analytes [1]. In this research, the dip-coating technique [2] is proposed as a rapid and simple way to coat the filter paper with polyvinyl chloride and post-modify it (see **Figure 1**). To do so, a piece of paper is immersed in a PVC solution, followed by solvent evaporation. The polymeric layer created over the paper surface is finally post-modified with diphenylamine by nucleophilic substitution. Thus, aromatic rings are deployed on the paper surface, making the interaction with the analytes by a mixed mode mechanism (comprising π-π and cation-π interactions) possible at physiological pH. The resulting material was characterized using infrared spectroscopy, UV-Vis spectroscopy, and scanning electron microscopy.

To evaluate the sorption capacity, the determination of three opioids (methadone, codeine, and tramadol) in saliva samples was proposed as the analytical problem, using direct infusion mass spectrometry to quantify them. Although the unmodified paper contributes to the extraction efficiency, the results demonstrated that the proposed modification increased the extraction selectivity and efficiency. Once the main variables involved in the extraction procedure were optimized (sample pH, extraction time, and sample dilution), the analytical characteristics of the method were assessed using blank saliva samples as the matrix. The proposed approach provided competitive limits of detection, as well as good linearity, precision, and accuracy. Finally, real saliva samples from patients undergoing codeine and tramadol treatment were analyzed, demonstrating the practical applicability of the developed method.

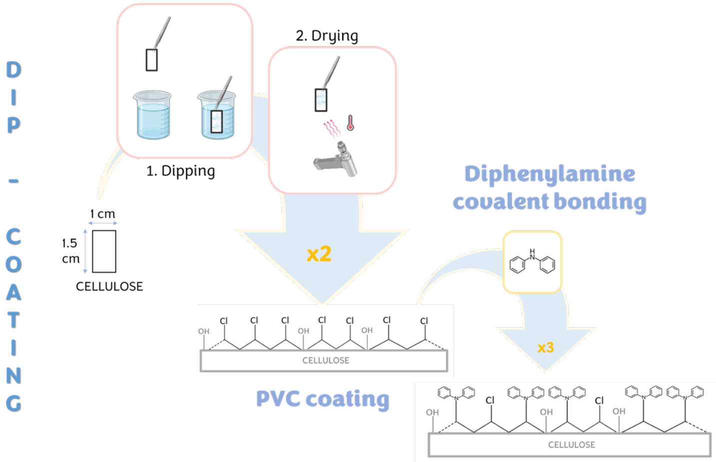

Figure 1. Scheme of the dip-coating technique used to modify the filter paper.

Acknowledgements

The research developed in this work has been possible thanks to the project PID2020-112862RB-I00 funded by MICIU/AEI/ 10.13039/501100011033 (Feder “Una manera de hacer Europa”). Ana M. Pedraza-Soto expressed her gratitude to the Ministry of Science, Innovation and Universities for the pre-doctoral grant FPU (Ref. FPU22/01752).

References

[1] M.C. Díaz-Liñán, R. Lucena, S. Cárdenas, A.I. López-Lorente, Unmodified cellulose filter paper, a sustainable and affordable sorbent for the isolation of biogenic amines from beer samples, J. Chromatogr. A 1651 (2021) 462297.
[2] X. Tang, X. Yan, Dip-coating for fibrous materials: mechanism, methods and applications, J. Sol-Gel Sci. Technol. 81 (2017) 378–404.

Strong Cation Exchange Microparticles Immobilized on Paper for the Selective Isolation of Opioids in Biofluids

PSD-08

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Keywords: *Cellulose, Direct infusion mass spectrometry, Mixed mode ionic exchange microparticles, Opioids, Thin-film microextraction*

Natural substrates, such as cellulose, are of great interest due to their availability, sustainability, and biodegradability [1]. The high porosity of cellulose paper provides a high surface area that makes possible the arrangement of particulate sorbents in a flat format, thus combining the advantages of both materials and fully exploiting the particles' capacity. In the present work, we propose filter paper as a sustainable substrate to immobilize commercial mixed-mode cation exchange microparticles (MCX) using polyacrylonitrile (PAN) as the binder. The dip coating technique was used to avoid complex modification procedures. The filter paper is just introduced in a slurry solution (PAN dissolved in N,N-dimethylformamide with dispersed MCX microparticles), followed by solvent evaporation. Thus, a polymeric layer with entrapped but accessible particles is formed over the paper. This results in a simple, fast, and cost-effective synthesis. Also, the procedure reduces the amount of sorbent material required, since 150 modified papers can be prepared with a single MCX cartridge.

The extraction efficiency has been evaluated by determining five opioids (codeine, methadone, naloxone, oxycodone, and tramadol), using direct-infusion mass spectrometry (DI-MS) for the quantification. The particles offer a mixed mode of interaction at physiological pH, combining reverse phase with ionic interactions due to the sulfonic groups, thus favoring the selective extraction of more polar analytes [2]. Once the synthesis and extraction procedures were optimized, the method was validated in terms of sensitivity, precision, and accuracy using blank saliva and urine samples. For the latter matrix, morphine was included as a target analyte since it is a codeine metabolite. Finally, real saliva and urine samples from volunteers under codeine treatment were analyzed, demonstrating the successful applicability of the method for biological sample preparation.

Acknowledgements

The research developed in this work has been possible thanks to the project PID2020-112862RB-I00 funded by MICIU/AEI/ 10.13039/501100011033 (Feder "Una manera de hacer Europa"). Ana M. Pedraza-Soto expressed her gratitude to the Ministry of Science, Innovation and Universities for the pre-doctoral grant FPU (Ref. FPU22/01752).

References

[1] M.C. Díaz-Liñán, R. Lucena, S. Cárdenas, A.I. López-Lorente, Unmodified cellulose filter paper, a sustainable and affordable sorbent for the isolation of biogenic amines from beer samples, J. Chromatogr. A 1651 (2021) 462297.

[2] C. Calero-Cañuelo, F.A. Casado-Carmona, R. Lucena, S. Cárdenas, Mixed-mode cationic exchange sorptive tapes combined with direct infusion mass spectrometry for determining opioids in saliva samples, J. Chromatogr. A 1702 (2023) 464097.

Use of Waste Plastics as Selective Supports for the Analysis of Cow's Milk Allergens

PSD-09

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Keywords: *α-Lactalbumin, Aptamer, Extraction, High-density polyethylene, Waste plastics*

Plastic waste is perceived as one of the major environmental problems since it is not biodegradable. One of the most used polymers in daily life is high-density polyethylene (HDPE), frequently found in chemical containers, or in water and shampoo bottles, among others. Since it is possible to easily modify the surface of waste HDPE plastics, they can be used as an attractive support for sample treatment producing a value-added material. Therefore, by properly modifying the HDPE plastic surface using ethylene glycol dimethacrylate as monomer, vinyl functionalities can be generated, allowing the subsequent attachment of specific ligands (such as aptamers). The resulting aptamer-based HDPE supports can serve as platforms for the extraction of target proteins, such as allergenic proteins from foods. Cow's milk allergy is an immunological response to cow's milk proteins such as casein, α-lactalbumin (α-LA) and β lactoglobulin. It is one of the most common food allergies, with a special prevalence in infants and children. Therefore, the development of efficient and reliable platforms with affinity sorbents able to detect target allergenic proteins even at trace levels is highly desirable from both consumers' safety and regulatory agencies.

In this work, aptamer-based HDPE plastic supports have been developed for extraction of α-LA, one of the main allergenic proteins present in milk and dairy products. The extraction units, based on HDPE plastic waste pieces, were firstly vinylized to subsequently immobilize a thiol-modified aptamer against α-LA via straightforward "thiol-ene" click chemistry. The resulting aptamer-based plastic supports were characterized, and several parameters that affect the extraction efficiency were optimized. Finally, the applicability of the method for determining low levels of α-LA was demonstrated by analyzing milk-free foods (*i.e.*, a hypoallergenic formula for infants, and dairy-free biscuits) as well as other milk-containing foods. The results highlighted several advantages for the developed aptamer-functionalized plastic platforms, including simple, low-cost, and eco-friendly preparation and operation, among others.

Acknowledgements
The authors acknowledge financial support from the Spanish State Research Agency (AEI//10.13039/501100011033/), the Spanish Ministry of Science, Innovation and Universities (MICIU) and the European Union (NextGenerationEU/PRTR) through projects PID2021-125459OB-I00. Also, the authors acknowledge the projects CIGE/2023/069 and CIAICO/2022/183 funded by Generalitat Valenciana. The authors extend their appreciation to MICINN for granting the Spanish Network of Excellence in Sample preparation (RED2022-134079-T). This communication is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society.

Development of an Affinity Sorbent in a Paper-Based Device for Lysozyme Extraction in Foods

PSD-10

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Keywords: *Allergenic protein, Aptamer, Cellulose paper, Lysozyme, Selective Sorbent*

Egg allergy is one of the most prevalent food allergies in infants. The primary egg allergens include ovalbumin, ovotransferrin, ovomucoid, lysozyme, and α-livetin. Specifically, lysozyme is a glycosidase that makes up 3.5% of the proteins found in egg white. To ensure consumers' safety, it is crucial to develop precise, sensitive and effective methodologies for detecting and quantifying egg allergenic proteins. In this regard, aptamers have been identified as innovative and stable recognition ligands, proving their effectiveness in various analytical applications due to their significant advantages in synthesis, modification and stability. They have demonstrated their utility in various analytical applications, particularly in the development of biosensors and as sorbents. However, the combination of aptamers with low-cost platforms based on sustainable materials, such as paper, has been scarcely explored. For these reasons, this work is focused on the development of paper-based devices modified with aptamers capable of recognizing the egg protein lysozyme. Firstly, a piece of paper was coated with a monolithic polymer based on 2-[(methacryloyloxy) ethyl] trimethylammonium chloride solution. During this initial stage, the volume of the polymerization mixture necessary to achieve a homogeneous and reproducible polymer coating was optimized. Next, the specific aptamer for lysozyme was immobilized on the surface of the polymer by adsorption. The aptamer was directly bound by DNA charge-dependent adsorption using the strong cationic quaternary ammonium-based monomer. Subsequently, the paper supports with the aptamer were used to extract lysozyme, evaluating several factors affecting the retention and elution of this protein. Once the optimal conditions were determined, the developed support was used to measure the lysozyme content in samples susceptible to containing traces of egg.

Acknowledgements

The authors acknowledge financial support from the Spanish State Research Agency (AEI//10.13039/501100011033/), the Spanish Ministry of Science, Innovation and Universities (MICIU) and the European Union (NextGenerationEU/PRTR) through project PID2021-125459OB-I00. Also, the authors acknowledge the projects CIGE/2023/069, CIAICO/2022/183 and INVEST/2022/107 funded by Generalitat Valenciana. The authors extend their appreciation to MICINN for granting the Spanish Network of Excellence in Sample preparation (RED2022-134079-T). This communication is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society.

Identification of Organic Compounds Released from 3D Printed Devices by GC-MS

PSD-11

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Keywords: *Chromatographic analysis, Ghost peaks, 3D-printing*

3D printing is a technique with many applications in different fields, including analytical chemistry. Among 3D printing techniques, fused deposition modelling (FDM) and stereolithography (SLA) are within the most widely used. In FDM printing a polymeric material is melted through a nozzle and deposited onto the platform. Unlike FDM, in SLA printing a liquid mixture of monomers of acrylates, urethanes or epoxides combined with a photoinitiator, is locally polymerized under a UV laser light on the printer platform [1]. Methodologies combining 3D printed devices for sample preparation with chromatographic separation and detection have been reported. Nevertheless, there is scarce information about the compounds that 3D devices may release when exposed to acids, solvents, and other substances inherent to analytical protocols. Some authors have reported the presence of ghost peaks when using 3D devices in HPLC-DAD methodologies [2]. Hence, the present study attempts to identify organic compounds released from 3D printed devices exposed to organic solvents by gas chromatography and mass spectrometer detector (GC-MS) exploiting NIST23 library for data analysis.

In total, six materials were selected for 3D printing: polylactic acid (PLA), polypropylene (PP), and nylon (NY) for FDM and Clear v4, Flexible 02 and Rigid 10k for SLA. The printing parameters varied in between the materials and the type of printing. After printing, each device was individually exposed to 5 mL of seven different solvents: 2-propanol (IPA), acetone (ACE), acetonitrile (ACN), dimethylformamide (DMF), ethanol (EtOH), methanol (MeOH), and tert-butyl methyl ether (TBME), under constant agitation at 200 rpm for 24 h. After exposure, the extract was filtered, reconstituted with hexane, and then injected into the GC-MS. The 3D devices printed with PLA didn't present enough structural resistance to ACE, ACN, and DMF. In addition, devices printed with Clear v4 resin were affected when exposed to DMF and ACE, and also the Flexible devices when exposed to DMF. Therefore, the leaching of organic compounds from the aforementioned materials has no reason, since they could not be used.

Among the identified compounds, 1-Hydroxycyclohexyl Phenyl Ketone and 2,4,6-Trimethylbenzoic acid, a photoinitiator [3] and a photolytic decomposition product [4], respectively, were found in the leaching profiles of SLA resins (**Figure 1**). In the case of FDM filaments the found compounds generally correspond to additives or material precursors. The results of this study will be of great help in the interpretation of chromatograms obtained through protocols that combine 3D devices and GC-MS analysis.

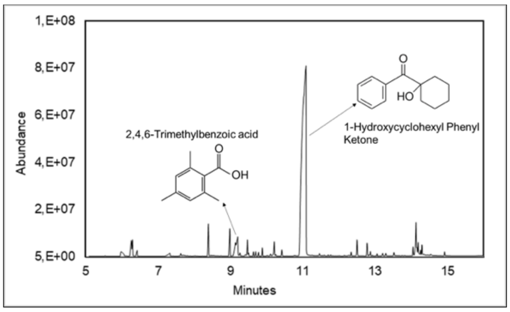

Figure 1. Chromatogram obtained of 3D device printed with clear v4 resin exposed to ACN.

Acknowledgements

Financial support from the Spanish Ministry of Science and Innovation, Agencia Estatal de Investigación (project PID2019-107604RB-I00/MCIN/AEI/ 10.13039/501100011033) is gratefully acknowledged. Brenda Mejía acknowledges the support from the CONAHCYT, Mexico and to the Advanced Materials Research Center for the pre-doctoral research fellowship.

References

[1] S.A. Monteiro, C. Scheid, M. Deon, J. Merib, Fundamentals, recent applications, and perspectives of 3D printing in sample preparation approaches, Microchemical Journal 195 (2023) 109385.
[2] D. Barzallo, E. Palacio, J. March, L. Ferrer, 3D printed device coated with solid-phase extraction resin for the on-site extraction of seven sulfonamides from environmental water samples preceding HPLC-DAD analysis, Microchemical Journal 190 (2023) 108609.
[3] I. Blinova, A. Lukjanova, H. Vija, M. Mortimer, M. Heinlaan, Toxicity of Plastic Additive 1-Hydroxycyclohexyl Phenyl Ketone (1-HCHPK) to Freshwater Microcrustaceans in Natural Water, Water 15 (2023) 3213.
[4] J.B. Scarsella, N. Zhang, T.G. Hartman, Identification and Migration Studies of Photolytic Decomposition Products of UV-Photoinitiators in Food Packaging, Molecules 24 (2019) 3592.

Comprehensive Analysis of Volatile Carbonyl Compounds in Wood-Based Panels Through Gas-Diffusion Microextraction Combined with HPLC-DAD

PSD-12

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Keywords: *Carbonyl compounds, GDME, Volatile organic compounds, Wood-based panels*

Wood-based panel (WBP) is a generic term for board products derived from fibres, particles, and/or veneers, which includes particleboards (PB), medium-density fibreboards, and plywood. Due to the wood material, chemical additives, and processes involved in their production, WBPs are known to emit volatile organic compounds (VOCs), which can impact indoor air quality and human health [1].

In this study, gas-diffusion microextraction (GDME), coupled with a derivatization reaction using 2,4-dinitrophenylhydrazine, was used to extract volatile carbonyl compounds from PB. Several studies were performed, such as the optimization of the GDME extraction parameters, evaluation of the method's precision, assessment of matrix effects, and more. The effect of different production parameters, such as the type of wood particle, resin, and moisture content, on the emission profile of volatile carbonyls from PB was assessed using principal component analysis (PCA). The results showed that GDME-HPLC-DAD could successfully differentiate PB according to their emission of carbonyl compounds, with differences being found for the type of resin used (urea-formaldehyde or UF fortified with melamine) and the nature of the wood particles used for PB production (pine and recycled) [2].

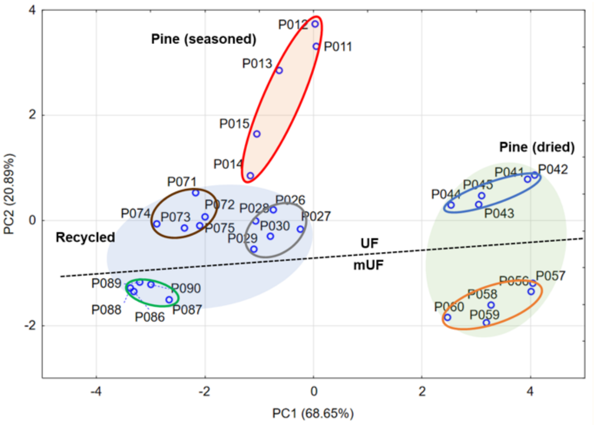

Figure 1. Graphical representation of PCA score scatterplots for PC1 and PC2, related to the GDME extraction of VOC from WBP.

Funding

This work received financial support from national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through project PTDC/CTM-PAM/1348/2021 (DOI: 10.54499/PTDC/CTM-PAM/1348/2021).

Acknowledgements

This work was supported by FCT/MCTES through national funds: LAQV, UIDB/50006/2020 (DOI: 10.54499/UIDB/50006/2020), UIDP/50006/2020 (DOI:10.54499/UIDP/50006/2020) and LA/P/0008/2020 (DOI: 10.54499/LA/P/0008/2020); LEPABE, UIDB/00511/2020 (DOI: 10.54499/UIDB/00511/2020) and UIDP/00511/2020 (DOI: 10.54499/UIDP/00511/2020) and ALiCE, LA/P/0045/2020 (DOI: 10.54499/LA/P/0045/2020). RMR acknowledges FCT for the Junior Research fellowship CEECIND/04259/2017 through the Individual Call to Scientific Employment Stimulus.

References

[1] T. Adamová, J. Hradecký, M. Pánek, Volatile Organic Compounds (VOCs) from Wood and Wood-Based Panels: Methods for Evaluation, Potential Health Risks, and Mitigation, Polymers 12 (2020) 2289.

[2] F.D. Gonçalves, M.L. Almeida, J.M. Martins, L.H. Carvalho, J.A. Rodrigues, R.M. Ramos, Gas-diffusion microextraction combined with HPLC-DAD for the comprehensive analysis of volatile carbonyl compounds in wood-based panels, Talanta 272 (2024) 125818.

Development of Low-Cost Extraction Platforms Modified with Metal-Organic Frameworks for the Analysis of Emerging Pollutants

PSD-13

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Keywords: *Cellulose paper, Metal-Organic Frameworks, Microextraction, Pollutants, 3D printing*

In the last years, the development of low-cost and sustainable extraction methods is considered one of the key nodal points in the research prioritization. In this sense, the use of new extraction devices manufactured using 3D printing has experimented a great increase in the sample preparation field, since they offer some advantages such as versatility in the materials to be used, low printing costs, flexibility in shape design, and purpose adaptation, among others. Also, 3D-printed extraction supports can be easily post-functionalized to immobilize different materials, thereby improving their performance. In addition to 3D-printed supports, other low-cost devices used for the extraction and determination of target analytes are paper-based supports, which can also be easily modified with various functional materials. One of the most widely used functional materials for extraction and removal of pollutants of emerging concern are metal-organic frameworks (MOFs), due to their large surface area, chemical stability, and versatility in tuning chemical composition and pore size. In any case, both types of extraction devices (3D-printed and paper-based platforms) can be combined with MOFs resulting in extraction devices with enhanced analytical performance.

This work proposes the development of sustainable extraction platforms (3D-printed and paper-based devices) modified with MOFs for the extraction of estrogens in environmental waters. After testing different MOFs using dispersive solid-phase extraction, the UiO-67(Zr) MOF was selected since it offered the best extraction performance of the considered estrogens. Therefore, after incorporation of UiO-67(Zr) in both 3D-printed and paper-based supports, different extraction parameters, such as loading and elution solvents, time of extraction and elution, among others, were optimized. Finally, the applicability of the developed extraction method is demonstrated by isolating and determining estrogens in environmental waters.

Acknowledgements

The authors acknowledge financial support from the Spanish State Research Agency (AEI//10.13039/501100011033/), the Spanish Ministry of Science, Innovation and Universities (MICIU) and the European Union (NextGenerationEU/PRTR) through projects PID2021-125459OB-I00. Also, the authors acknowledge the projects CIGE/2023/069 and CIAICO/2022/183 funded by Generalitat Valenciana. The authors extend their appreciation to MICINN for granting the Spanish Network of Excellence in Sample preparation (RED2022-134079-T). This communication is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society. This study forms part of the Advanced Materials programme and was supported by MCIN with funding from European Union NextGenerationEU (PRTR-C17.I1) and by Generalitat Valenciana.

GC×GC Analysis of Organics Leached from Cigarettes and Heat-not-Burn Tobacco Products

PSD-14

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Keywords: *Cigarette butts, Leachates, HiSorb, TD-GC×GC-MS*

Cigarette butts constitute the main type of litter collected from both urban areas and coasts worldwide [1]. Improperly discarded tobacco products have been proven to leach a variety of toxic and potentially carcinogenic chemicals, such as polycyclic aromatic hydrocarbons (PAHs), heavy metals, as well as nicotine, aromatic amines, nitrosamines, phenols, and BTEX (benzene, toluene, ethyl-benzene & xylene) [1,2,3]. This study aims to detect and compare the leached compounds from unused and used conventional cigarettes (CCs) and heat-not-burn tobacco sticks (HnBs), using High-Capacity Sorptive Extraction (HiSorb) followed by Thermal Desorption (TD) and comprehensive two-dimensional Gas Chromatography (GC×GC) coupled to Mass Spectrometry (MS) to assess their environmental risk.

Four different types of leachates were prepared in ultrapure water by soaking unused or used HnBs and CCs at a 10 L kg^{-1} liquid-to-solid ratio for 24 hours at room temperature (25°C). Subsequently, 9 mL of each leachate was transferred to 10 mL vials and HiSorb units with Polydimethylsiloxane (PDMS) coating were directly immersed (DI) in the samples for 1 hour at 30°C and 300 rpm. After extraction, the probes were thermally desorbed at 250°C for 10 min and compounds separation occurred in a GC×GC using a combination of a low-polar and a mid-polar column, linked by a flow modulator with a 5 sec modulation period. MS scan range was set from 40 to 550 m/z.

The two most abundant chemicals detected across all four leachate types are triacetin, used as an additive in tobacco during the production to augment its combustion propensity, and nicotine, a naturally occurring toxic alkaloid in the tobacco plant. Additional tobacco alkaloids consistently found in the samples are myosmine, nicotyrine and 2,3'-dipyridyl. Overall, smoked CCs released significantly more organic compounds into water compared to operated HnBs. In used CCs leachates, nitrogen-containing compounds such as unsubstituted and alkyl derivatives of pyridine, pyrrole, indole, quinoline and benzonitrile were widely abundant. Notably, pyridine and its C1- to C5- alkyl pyridine homologues emerged as the most prominent class. Oxygen-containing compound groups were also detected in used CCs, including unsubstituted and alkylated analogues of phenol, indanone, furfural derivatives and cyclohexanone. These chemical classes were far less abundant or not detectable in operated HnBs and the control leachates of unused tobacco products. Considering that CCs smoking takes place at temperatures above 600°C, in contrast to HnBs heating at 350°C, and given that several compounds from the detected chemical classes have been previously proposed as combustion by-products of major tobacco alkaloids, it is indicated that detected analogues are also by-products of this thermal process. Regarding the extraction and analysis methods, HiSorb probe's large stationary phase volume (65uL), facilitates effective extraction at mild temperatures and combined TD-GC×GC-MS, it significantly enhances the detection of hazardous chemicals from highly complex matrices, such as leachates from used tobacco products. Untargeted analysis benefits from the increased peak capacity of GC×GC, as it significantly improves the resolution of peaks that would otherwise co-elute in one-dimensional GC analysis, allowing maximum insight into sample composition.

Acknowledgements
The authors wish to thank A.C. Laskaridis Charitable Foundation for the PhD scholarship. They also extend their gratitude to Markes Ltd for providing the HiSorb probes and SepSolve and Shimadzu Europa GmbH for their continuous support.

References

[1] N. Solomou, E. Fernández, R. Szafnauer, E. Psillakis, Total and bioavailable polycyclic aromatic hydrocarbons in unused and operated heat-not-burn tobacco products and conventional cigarettes, Chemosphere 335 (2023) 139050.
[2] F. Soleimani, S. Dobaradaran, G.E. De-la-Torre, T.C. Schmidt, R. Saeedi, Content of toxic components of cigarette, cigarette smoke vs cigarette butts: A comprehensive systematic review, Sci. Total Environ. 813 (2022) 152667.
[3] N. Koutela, E. Fernández, M.L. Saru, E. Psillakis, A comprehensive study on the leaching of metals from heated tobacco sticks and cigarettes in water and natural waters, Sci. Total Environ. 714 (2020) 136700.

Green Multi-Residue Pesticide Extraction from Food Samples Using Natural Deep Eutectic Solvents

PSD-15

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Keywords: *Food safety, Green sample preparation, NADES, Pesticides*

Natural deep eutectic solvents (NADES) have recently emerged as a promising alternative to conventional solvents since they present several advantages such as their biodegradability, low cost, high stability and low toxicity. NADES are composed of natural components (primary metabolites) such as sugars, alcohols, amino acids, organic acids, and choline derivatives that, at a specific molar ratio composition, present a significant melting point depression and become liquids [1]. NADES are suitable for the development of new sample extraction options aligned with the green sample preparation principles and new trends in green analytical chemistry [2]. Although, they have been mostly used to extract biologically active compounds, there is a growing interest in their application for the extraction of contaminants such as pesticides.

In this work, we investigated the applicability of NADES for multiclass pesticides extraction prior to their determination by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). For this, the assessment of several hydrophilic and hydrophobic NADES as extraction solvents for 11 model pesticides (omethoate, acetamiprid, propamocarb, metoxuron, azoxystrobin, cyprodinil, tebuconazole, spinosyn A & D, chlorpyrifos and deltamethrin) from different food samples such as spinach, orange and wheat were studied. The selected pesticides, including fungicides, herbicides and insecticides, belong to different chemical classes and present a wide spectrum of physicochemical properties. In the same way, the selected target matrices represented various commodity groups: group 1 (high water content), group 2 (high acid and high water contents) and commodity group 5 (high starch and/or protein and low water and fat contents).

The NADES were also tailored to cover a wide range of physicochemical properties such as polarity, pH and viscosity, which plays an important role in extraction efficiency. The composition of each NADES as well as the molar ratio of the components were carefully selected. The following NADES were prepared by the heating and stirring method and evaluated as extraction solvents: lactic acid:glycerol:water (1:1:3), urea:glycerol:water (1:3:2.5), betaine:lactic acid:water (1:1:3.5), thymol:menthol (1:1) and dodecanoic acid:menthol (1:4). It is worth to mention, that all tested NADES were previously characterized by Nuclear Magnetic Resonance (NMR) and Fourier-Transform Infrared (FTIR) spectroscopy to confirm the formation of the supramolecular structure of the eutectic mixture.

After the solid-liquid extraction of the different food commodities with the these NADES, the results showed that, in general, they have a potential applicability as extraction solvents. Nevertheless, certain NADES appeared to be less compatible with chromatography evidenced by peak broadening or higher matrix effects for some target compounds. Taking these aspects into account, as well as the highest recoveries obtained across the target pesticides and matrices, the hydrophobic NADES composed of thymol: menthol (1:1) proved the most favourable and was selected for further experiments. Other variables affecting the extraction efficiency such as the addition of water, pH and extraction time were also evaluated. In most cases, it provided recoveries above 70 % and matrix effects below 20 % across all the studied matrices. In addition, the greenness of the proposed sample treatment was assessed by the AGREEprep metric tool, highlighting the sustainability of the procedure. Furthermore, the practicality and applicability of the method was evaluated by the blue applicability grade index (BAGI). Finally, the optimized method was validated for a greater number of related pesticides in spinach, orange and wheat samples following the SANTE/11312/2021 guidance [3].

To sum up, the proposed method demonstrated that NADES can be applied in multiresidue pesticides analysis with a great potential to be implemented into routine analysis, thereby reducing costs, environmental impacts and hazards to operators.

Acknowledgements

LCR thanks the "Juan de la Cierva" postdoc program (FJC2021-047728-I) funded by the Spanish Ministry of Science and Innovation MCIN/AEI/10.13039/501100011033 and the European Union "NextGenerationEU"/PRTR".

References

[1] A. Paiva, R. Craveiro, I. Aroso, M. Martins, R.L. Reis, A.R.C. Duarte. Natural deep eutectic solvents – solvents for the 21st century. ACS Sustain Chem. 2(5) (2014) 1063-1071.

[2] A.I. López-Lorente, F. Pena-Pereira, S.Pedersen-Bjergaard, V.G. Zuin, S.A. Ozkan, E. Psillakis, The ten principles of green sample preparation. TrAC Trends in Analytical Chemistry 148 (2022) 116530.

[3] SANTE/11312/2021 guidance (V2). Analytical quality control and method validation procedures for pesticide residues analysis in food and feed.

Hydrocarbon Oil Index: Scale Down Approach for Automation of C10-C40 According to UNI EN ISO 9377-2

PSD-16

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Keywords: *Green chemistry, Hydrocarbon in water analysis, C10C40, Sample prep automation, Solvent saving*

Current Italian regulation on environmental protection asks, in various areas, for the determination of mineral oils.
In particular, Legislative Decree 152/06 reports threshold values for this parameter for different aqueous matrices. The currently most widespread method (UNI EN ISO 9377-2), involves the extraction of 900 ml of sample with more than 50 ml of hexane, requires several time-consuming steps like Dehydration of the extract and purification on florisil®, and mandatorily needs a concentration process; such workflows is prone to random errors and, more important, constitute a potential source of continuous and prolonged exposure of operators to chemical vapors.
In this poster, it is demonstrated the possibility to operate a completely automated scale-down, avoiding any concentration step and automating the whole workflow, including florisil® cleanup.
The analytical platform developed by SRA allows to:

- Reduce the amount of sample needed for analysis over an order of magnitude
- Limit the volume of solvent to less than 2 ml per sample
- Automate the entire process with no need of any operator attendance
- Avoid the evaporation phase
- Meet, and even improve, the requirements of the official method, including LOQ/LOD
- Eliminate any operator's solvent exposure

Thus ensuring greater productivity, while reducing random errors thanks to the complete automation of the entire process.

Developing Preanalytical Method for the Extraction and Preconcentration of Non-Steroidal Anti-Inflammatory Drugs from Wastewater Samples Using Ionic Liquid-Based Aqueous Biphasic Systems

PSD-17

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Keywords: *Aqueous biphasic systems, Ionic liquid, NSAID, Pretreatment*

The presence of non-steroidal anti-inflammatory drugs (NSAIDs) such as naproxen, nimesulide, ibuprofen, and diclofenac in aquatic environments has sparked significant environmental and health concerns due to their ability to accumulate in organisms and their potential for long-term exposure [1]. Detecting these compounds pose challenges due to their typically low concentrations in water bodies. Consequently, developing alternative methods for their simultaneous extraction and concentration from aqueous samples is imperative. This study delves into the utilization of an aqueous biphasic system (ABS) composed of tetrabutylphosphonium salicylate ionic liquid [TBP][Sal] and citrate salt to concentrate these NSAIDs from aqueous samples. Initially, the liquid-liquid equilibria of the ABS were examined at various temperatures [2], and extraction conditions (ABS composition and temperature) were established. Remarkable one-step extraction efficiencies of NSAIDs, nearing 100%, were achieved. Additionally, the impact of varying amounts of ionic liquid and salt on extraction efficiency and preconcentration factors was systematically investigated. Furthermore, the preconcentration factors of NSAIDs were fine-tuned through strategic adjustments of the phase-forming component compositions to tailor the volumes of the coexisting phases. In terms of designing a pretreatment protocol, meticulous planning and adjustment of the extraction conditions and ABS composition are crucial steps for maximizing efficiency while minimizing the consumption of ABS constituents, ionic liquid, and salt. This optimization can significantly cut costs and enhance process feasibility. Preconcentration factors of up to 1500-fold for NSAIDs were attained in a single-step process, without reaching saturation of the IL-rich phase (**Figure 1**).

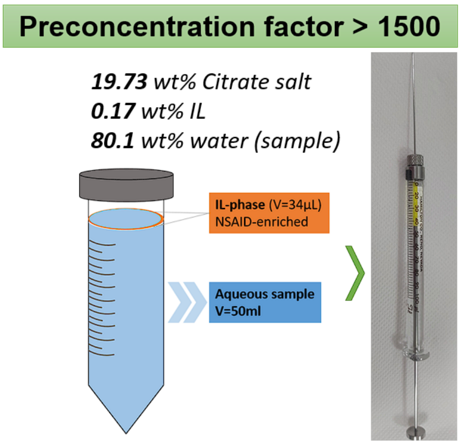

Figure 1. Representation of aqueous biphasic systems for NSAID extraction from aqueous samples.

This level of preconcentration, up to μg L^{-1}, facilitated the straightforward identification and quantification of NSAIDs using a High-Performance Liquid Chromatography (HPLC) system coupled with a UV detector, for both model systems (distilled water) and real effluent samples from a wastewater treatment plant. This research underscores the critical role of preconcentration in pretreatment processes, offering a robust method for enhancing the monitoring and environmental analysis of NSAIDs in water samples.

Acknowledgements
This work was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Contract number: 451-03-66/2024-03/200017 from 05 February 2024).

References

[1] M.J. Benotti, R.A. Trenholm, B.J. Vanderford, J.C. Holady, B.D. Stanford, S.A. Snyder, Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water, Environ. Sci. Technol. 43 (2009) 597–603.
[2] M.G. Freire, A.F.M. Cláudio, J.M.M. Araújo, J.A.P. Coutinho, I.M. Marrucho, J.N.C. Lopes, L.P.N. Rebelo, Aqueous biphasic systems: a boost brought about by using ionic liquids, Chem. Soc. Rev. 41 (2012) 4966-4995.

In-Syringe Dispersive Solid Phase Extraction of Selected Alkyl-Phenols Coupled Online to HPLC

PSD-18

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Keywords: *Alkyl-phenols, High performance liquid chromatography, Iron (III) thenoyltrifluoroacetonate complex, Lab-in-syringe automation, Solvent-assisted dispersive solid phase extraction*

An overview of developing a new eco-friendly and fully automated method for the preconcentration of selected alkylphenols namely 4-nonylphenol, 4-heptylphenol, and 4-tert octylphenol, in water samples will be presented. The method was based on solvent-assisted dispersive micro-solid phase extraction, which was automated via the flow-batch technique Lab-In-Syringe (LIS) [1] and coupled online to HPLC equipped with diode array detection. In LIS system, the void of a glass syringe is used as mixing and extraction vessel on a computer-controlled bidirectional syringe pump with multiposition head valve. This way, the entire solvent-assisted dispersive micro solid phase extraction procedure can be carried out in automate fashion. Iron (III) thenoyltrifluoroacetonate complex [2], was used for a novel dissolvable sorbent for extraction of alkylphenols for the first time. A small volume of pre-dissolved sorbent was dispersed in the sample solution inside the void of an automatic syringe pump upon which it precipitated and yielded a solid nanostructured sorbent. The extraction occurred by analyte adsorption within 40 s, which was accelerated by in-syringe magnetic stirring. Then, the sample was discharged while the sorbent including analytes were retained on a low flow resistance melamine foam inserted in the syringe inlet. Afterwards, the sorbent was dissolved together with the analytes using a methanolic eluent that subsequently was directly injected to HPLC. Parameters influencing the method including the extraction pH, volume of sorbent solution, stirring rate, sample volume, extraction time, eluent volume, and transfer volume to HPLC were optimized. Moreover, the HPLC method was optimized to obtain baseline separation of the listed analytes and sorbent components and validated. Under optimum conditions, linear dynamic ranges were confirmed from 5 µg L^{-1} to 1000 µg L^{-1} ($R^2 > 0.997$) with limits of detection (LOD) ranging from 0.5 µg L^{-1} to 0.9 µg L^{-1}. The developed and validated method was successfully implemented for the analysis of the selected alkylphenols in spiked water samples. The developed method complies a green approach to sample preparation fulfilling the following characteristics: preconcentration factor around 17 to improve the sensitivity, fast extraction, low solvent consumption, minimum waste generation and online connection with chromatographic separation [3].

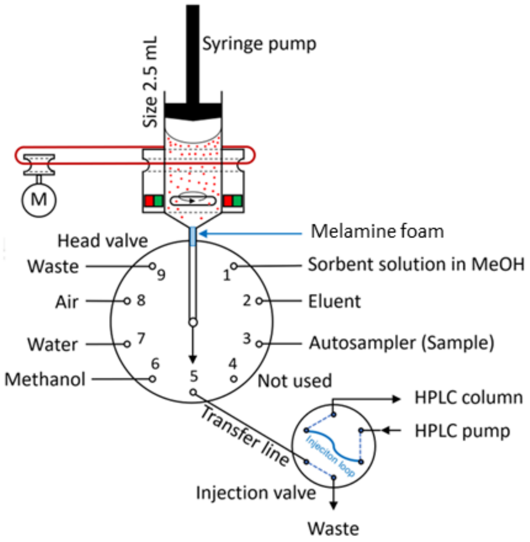

Figure 1. Scheme of Lab-In-Syringe system for automated solvent-assisted dispersive SPE.

Acknowledgements
This study was supported by specific research project SVV 260 662 and GAUK project 206623.

References
[1] B. Horstkotte, P. Solich, The automation technique lab-in-syringe: A practical guide, Molecules, 25(7) (2020) 1612.
[2] C.V. Gemuh, et al., Solvent-assisted dispersive micro-solid phase extraction of bisphenols using iron(iii) thenoyltrifluoroacetonate complex (Fe (TTA)3) as a new nanostructured sorbent: a proof of concept, Anal. Methods, 15 (2023) 2061–2072.
[3] Á.I. López-Lorente, et al., The ten principles of green sample preparation, Trends Anal. Chem. 148 (2022) 116530.

New Developments for MOSH/MOAH Automated Analysis

PSD-19

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Keywords: *Food contact materials (FCM), LC-GC hyphenation, Mineral oil hydrocarbons, MOSH, MOAH*

In 2023 the European Food Safety Agency (EFSA) expert panel provisionally concluded about mineral oil hydrocarbons (MOH) that the saturated hydrocarbons (MOSH) do not pose a health concern [1]. They also confirmed that some substances of the mineral oil aromatic hydrocarbons (MOAH) in MOH are still a possible health concern. Thus, the reliable quantification of a sample's MOAH content in food and food contact materials (FCM) received particular importance for the food safety assessment.

The MOSH/MOAH analysis requires the separation of the saturated hydrocarbons from the lower level cancerogenic aromatic compounds. A chromatographic separation can only be achieved by normal phase liquid chromatography. A separation of saturated and aromatic compounds on GC is not possible. The separately eluting LC fractions of MOSH and MOAH compounds are online transferred to GC for determination. Each fraction is directed into dedicated GC columns and detected in parallel by FID. The presented workflow includes the removal of biogenic interferences from alkanes by an integrated aluminum oxide clean-up and from natural olefins by a proprietary epoxidation step to avoid the overestimation of the critical MOAH content [2]. The peak integration, quantitation and reporting require the integration of certain C-chain windows that is achieved by a MOSH/MOAH specialized software for the EFSA compliant reporting [3].

The automated sample preparation with the online LC, integrated clean-up steps and online fraction transfer to GC for MOSH/MOAH analyses represents a true green analytical method with only low solvent use, avoiding consumables and operator exposure to chemicals, compared to a manual solid phase extraction (SPE) procedure [4].

The fully automated turnkey method providing the most recent workflow developments using the CHRONECT PAL System is presented. The analysis follows the international regulations and standards and is in use in governmental, industrial and private laboratories globally.

References

[1] Schrenk, Dieter, Margherita Bignami, Laurent Bodin, Jesús del Mazo, Bettina Grasl-Kraupp, Christer Hogstrand, Laurentius Hoogenboom, et al. 2023. "Update of the Risk Assessment of Mineral Oil Hydrocarbons in Food." EFSA Journal 21 (9): 143. https://doi.org/10.2903/j.efsa.2023.8215

[2] Nestola, Marco. 2022. "Automated Workflow Utilizing Saponification and Improved Epoxidation for the Sensitive Determination of Mineral Oil Saturated and Aromatic Hydrocarbons in Edible Oils and Fats." Journal of Chromatography A 1682: 463523. https://doi.org/10.1016/j.chroma.2022.463523

[3] Bratinova, Stefanka, and Eddo Hoekestra. 2019. Guidance on Sampling, Analysis and Data Reporting for the Monitoring of Mineral Oil Hydrocarbons in Food and Food Contact Materials. Edited by Stefanka Bratinova and Eddo Hoekestra. Ispra (VA), Italy: European Commission, Joint Research Centre (JRC). https://doi.org/10.2760/208879

[4] Bundesinstitut für Risikobewertung. 2012. "Determination of Hydrocarbons from Mineral Oil (MOSH & MOAH) or Plastics (POSH & PAO) in Packaging Materials and Dry Foodstuffs by Solid Phase Extraction and GC-FID." http://www.bfr.bund.de/cm/349/determination-of-hydrocarbons-from-mineral-oil-or-plastics.pdf

Green Approach Strategy Using Aqueous Biphasic Systems with Ionic Liquids as Pre-Treatment Method for Pesticide Determination in Food Sample

PSD-20

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Keywords: *Aqueous biphasic systems, Ionic liquid, Pesticide, Preconcentration*

The pesticide residues in foods have received increasing attention as one of the most important food safety issues [1]. Therefore, more strict regulations on the maximum residue limits for pesticides in foods have been established in many countries and health organizations. However, the analysis of pesticide residues is a continuing challenge mainly because of the small quantities of analytes as well as the large amounts of interfering substances which can be co-extracted with them, often leading to experimental errors. Therefore, the development of alternative pre-treatment techniques for their extraction and preconcentration from food samples is a crucial requirement.

In this work, we proposed a new green approach for pesticide extraction and preconcentration from food samples based on ionic-liquid-based aqueous biphasic systems (IL-based ABS). Aqueous biphasic systems (ABS) are an environmentally safe alternative to classic liquid-liquid extraction (LLE) and can be formed by mixing aqueous solutions of two water-soluble components at appropriate concentrations or a particular temperature [2]. Ionic liquids (ILs) are organic salts with unique properties such as liquid states at low temperatures, negligible vapor pressure, and high thermal stability, and they have been strategically introduced as components to ABS as novel, greener solvents [2].

ABS composed of tetrabutylammonium ILs (tetrabutylammonium salicylate [TBA][Sal], tetrabutylammonium acetate [TBA][Ac], and tetrabutylammonium lactate [TBA][Lac]) and ammonium sulfate salt were tested for the single-step extraction and enrichment of two pesticides with different polarities: deltamethrin (DLT), a nonpolar pyrethroid insecticide and pyraclostrobin (PYR), a moderately polar strobilurin fungicide. All IL-ABSs demonstrated high extraction efficiencies for both pesticides into the IL-rich phase (**Figure 1**). [TBA][Sal] with ammonium sulfate showed an extraordinary ability to form ABS with considerably low amounts of phase-formers, achieving extraction efficiencies of over 80% using 20 wt% of IL and less than 3 wt% of salting-out agent.

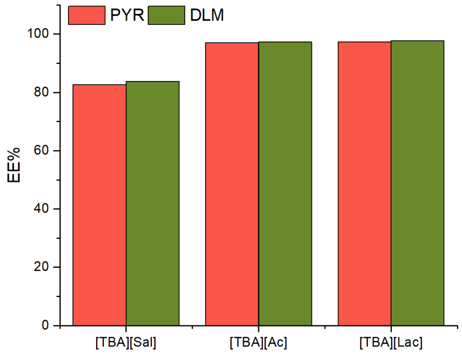

Figure 1. Extraction efficiencies of ABS composed of IL + $(NH_4)_2SO_4$ + H_2O at 25 °C for pesticides.

The [TBA][Sal] system was further optimized because its lower required concentrations of constituents align better with green chemistry principles by reducing overall chemical usage and minimizing environmental impact. By appropriately manipulating the compositions of the phase-forming components to tailor the volumes of the coexisting phases, high preconcentration factors for both pesticides were achieved in a single-step process. The preconcentration of pesticides up to mg L^{-1} allowed their easy and straightforward identification and quantification by HPLC or other methods.

The optimized IL-ABS system was successfully applied to strawberries spiked with pesticides, demonstrating its practical application for real food samples. This study underscores the potential of IL-ABS as an efficient and sustainable platform for pesticide extraction and preconcentration, offering considerable advantages over traditional methods in terms of environmental safety and operational efficiency.

Acknowledgements

This work was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Contract number: 451-03-66/2024-03/200017 from 05 February 2024).

References

[1] U. Bajwa, K.S. Sandhu, Effect of handling and processing on pesticide residues in food- a review, J. Food Sci. Technol. 51 (2014) 201-220.

[2] M.G. Freire, A.F.M. Cláudio, J.M.M. Araújo, J.A.P. Coutinho, I.M. Marrucho, J.N.C. Lopes, L.P.N. Rebelo, Aqueous biphasic systems: a boost brought about by using ionic liquids, Chem. Soc. Rev. 41 (2012) 4966-4995

Green Extraction of Pesticides in Pear by Matrix Solid Phase Dispersion Combined with Natural Deep Eutectic Solvents

PSD-21

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Keywords: *LC-MS/MS, Matrix-solid phased dispersion, Natural deep eutectic solvent, Pear*

Pears are a tasty and healthy fruit that is widely consumed around the world. To make their production profitable, pesticides are usually used both while the pears are growing on the tree and after they are harvested. These pesticides can remain in the fruit, sometimes at concentrations above the maximum residue levels (MRLs), posing a health risk to the consumer. It is therefore essential to control the presence of pesticides in pears before they are placed on the market. Accordingly, in the present work and taking into account the principles of green analytical chemistry, the use of natural deep eutectic solvents (NADES), as an alternative to conventional and toxic organic solvents, was evaluated as eluent after matrix solid-phase dispersion of seven pesticides (thiametoxam, acetamiprid, pirimicarb, thiacloprid, tebuconazole, difenoconazole and pyriproxyfen) in pear samples (peel and pulp). Final determination of target analytes was performed by high-performance liquid chromatography-tandem mass spectrometry (LC-MS/MS).
Choline chloride-based NADES with different hydrogen bond donors (carboxylic acids and alcohols) and different dispersant sorbents (alumina, florisil, PSA and octadecylsilica) were tested. Other variables such as NADES volume, sample-dispersant ratio, application of agitation and/or sonication were optimised to achieve quantitative recoveries for all target pesticides at concentrations lower than the corresponding established MRLs.

Acknowledgements
The Grant PID2021-122327OB-I00 funded by MCIN/AEI/ 10.13039/501100011033 and by “ERDF A way of making Europe” is gratefully acknowledged. This communication is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society and the National Thematic Network on Sustainable Sample Treatment (RED2022-134079-T) funded by the Spanish Ministry of Science and Innovation.

A Composite Cryogel Embedded in a Needle Hub for Miniaturized In-Syringe Solid Phase Extraction of Preservatives in Beverage Samples Followed by HPLC-DAD Analysis

PSD-22

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Keywords: *Food preservatives, High-performance liquid chromatography, In-syringe solid phase extraction, Miniaturized sample preparation, Porous composite adsorbent*

A hierarchically porous adsorbent of polyethylene dioxythiophene (PEDOT) embedded in a polyvinyl alcohol cryogel was fabricated in a needle hub and applied for the in-syringe solid phase extraction of parabens in beverages. A hierarchical pore system was generated through a reaction between hydrochloric acid solution and calcium carbonate, which was introduced during the cryogel synthesis within a needle hub. The porosity of the cryogel facilitated the entrapment of adsorption materials, multiplying adsorption sites, and PEDOT enhanced the adsorption of parabens through hydrophobic and π-π interactions. The composite adsorbent was characterized, and the extraction conditions were optimized. The extracted parabens were determined by high-performance liquid chromatography. Under optimized conditions, the developed method provided limits of detection ranging from 0.15 to 0.25 μg L^{-1} and limits of quantification ranging from 0.50 to 1.0 μg L^{-1}. The developed method successfully determined parabens in various beverage samples with extraction recoveries between 88.4% and 98.4% and RSDs below 6%. The extraction efficiency of the developed method was compared with the performance of a commercial sorbent for conventional solid phase extraction. The in-syringe extraction approach proved to be a convenient method, and the composite adsorbent demonstrated ease of preparation, good reproducibility, and reusability for twelve extraction-desorption cycles.

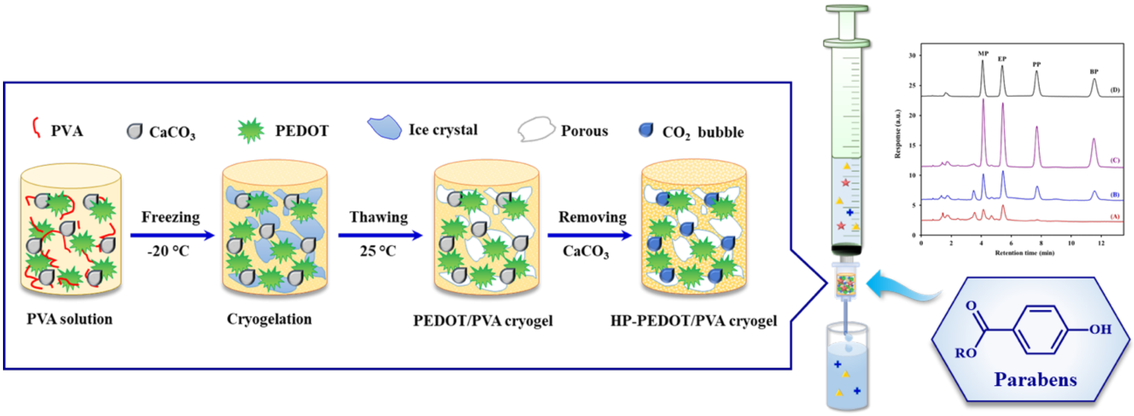

Figure 1. Fabrication of composite adsorbent and in-syringe solid phase extraction device for the extraction of parabens.

Experimental Design and Optimization of the Fabric Phase Sorptive Extraction of Anti-Diabetic Drugs in Water

PSD-23

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Keywords: *Anti-diabetic drugs, Fabric phase sorptive extraction, Water*

Pharmaceuticals such as anti-diabetic drugs are considered as contaminants of emerging concern which could have environmental and health impact. Fabric Phase Sorptive Extraction (FPSE) is a promising sample preparation method before the analysis of these contaminants [1]. In this study, FPSE was explored for the high-performance liquid chromatography- photodiode array (HPLC-PDA) analysis of ten anti-diabetic drugs (metformin, dapagliflozin, pioglitazone, gliclazide, glimepiride, liraglutide, vildagliptin, glargine, sitagliptin, and repaglinide) in water. Preliminary experiments showed that FPSE material (1 cm diameter) made from glass fiber (GF) and polyethylene glycol (PEG-300) and no further sample pH adjustment were suitable for the simultaneous extraction of ten anti-diabetic drugs. The optimum conditions for the extraction were determined by employing Box-Behnken Design (BBD) and Response Surface Methodology (RSM) for the FPSE adsorption and elution. A total of 30 experiments (15 each for adsorption and elution) were conducted with sample volume (1, 3, 5 mL), ionic strength (0, 1, 2% NaCl), and adsorption time (15, 30, 45 min); and elution solvent (50, 75, 100% acetonitrile(ACN):methanol(MeOH), elution volume (0.2, 0.6, 1 mL), and elution time (10, 20, 30 min) as independent variables for the adsorption and elution, respectively. The average adsorption efficiencies (%) and average recoveries (%) were used as the dependent variables. According to ANOVA and Pareto Charts, the sample volume and elution volume were significant. RSM revealed that adsorption efficiencies are maximized when lower sample volume, no salt adjustment, and longer adsorption time are used. For the elution, RSM has shown that maximum recoveries can be obtained using higher volume of solvent, higher %ACN, and shorter elution time. Based on these results and the chromatographic patterns, the optimum conditions were determined to be 1 mL sample volume, 0% ionic strength, and 45 min for the adsorption; and 1 mL solvent, 100% ACN, and 10 min for the elution. The optimized FPSE conditions can be applied prior to the HPLC-PDA analysis of anti-diabetic drugs in water samples. The determination of the concentrations of anti-diabetic drugs in water samples is one of the initial steps in assessing the impact of these drugs to the environment.

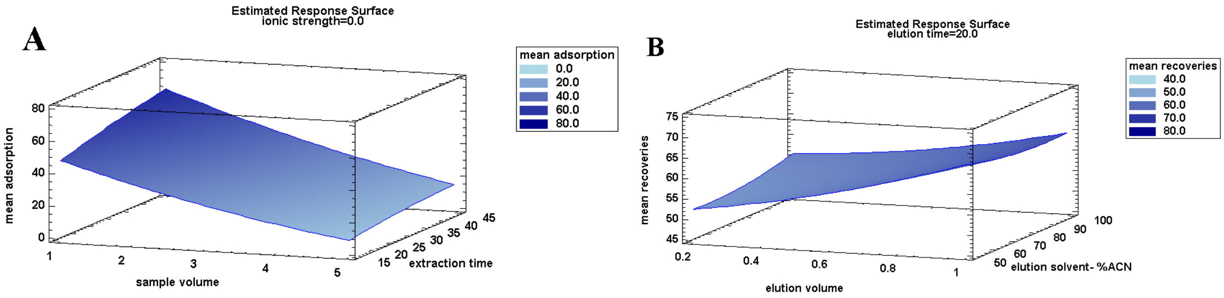

Figure 1. Response surface plots (A- adsorption and B- elution) of the BBD and RSM for the FPSE of ten anti-diabetic drugs in water.

Acknowledgements
This research is funded under the European Union’s HORIZON- Marie Skłodowska-Curie Action (MSCA) Project Nº 101119555: Human footprint on water from remote cold areas to the tropical belt. Integrated Approach TO secure water QUAlity by exploiting Sustainable processes (IN2AQUAS).

Reference

[1] N. Fontanals, F. Borrull, R.M. Marcé, Fabric phase sorptive extraction for environmental samples, Adv. Sample Prep. 5 (2023) 100050.

3D Printed Device for In-Situ Solid-Phase Extraction of Six NSAIDs from Wastewater and Subsequent Analysis by UPLC-DAD/FLD

PSD-24

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Keywords: *3D printing, In-situ extraction, NSAIDs, UPLC, Wastewater*

Non-Steroidal Anti-Inflammatory Drugs (NSAIDs) are over-the-counter medications widely consumed for their anti-inflammatory and antipyretic attributes. Predominantly utilized NSAIDs include ibuprofen, diclofenac, and naproxen, which has been detected in the effluents of wastewater treatment plants (WWTP), and many environmental matrices as rivers, lakes and even oceans [1]. Monitoring of NSAIDs in the environment is therefore of the utmost importance, as they are even classified as emerging pollutants [2]. Therefore, developing methodologies capable of performing in-situ sampling will help their environmental control, avoiding sample transportation which can pose challenges due to space constraints or the required pretreatment for preservation [3]. This work presents a new methodology for the on-site extraction of six selected NSAIDs (acetylsalicylic acid, celecoxib, diclofenac, ibuprofen, ketoprofen and naproxen) from water samples, followed by a chromatographic separation using UPLC-DAD/FLD. FLD was used because of its high sensitivity and specificity of the native fluorescence, while DAD was employed for diclofenac determination, avoiding the derivatization required by FDL. Two pieces have been designed and 3D printed by stereolithographic technique, (i) one used as a support to be coated with Oasis HLB resin for the selective solid-phase extraction (SPE) and pre-concentration of this type of compounds (Fig.1a), and (ii) another to contain the above extraction device and allow the flow-based sampling helped by portable pump (Fig.1b). The detection and quantification limits of the method were respectively as follows: 0.2 and 0.5 μg/L for acetylsalicylic acid, 0.2 and 0.8 μg/L for celecoxib, 1.5 and 4.9 μg/L for diclofenac, 0.2 and 0.8 μg/L for ibuprofen, 0.1 and 0.4 μg/L for ketoprofen and, finally, 0.3 and 1.0 μg/L for naproxen. The inter- and intra-day precisions were lesser than 5% (RSD). 3D printed coated devices can be reused up to 24 times without significant loss of extraction efficiency, achieved by maintaining the coating as observed through SEM images (Fig.1c and d). The on-site extraction was carried out at the Calvià WWTP (Mallorca, Spain), where the six NSAIDs were found at the inlet of the primary decanter, and at the outlets of the secondary decanter and the tertiary treatment, demonstrating the viability of the on-site extraction over a wide range of concentrations. Although the results of addition/recovery tests have been satisfactory (recoveries >91%) for celecoxib, diclofenac, ibuprofen, ketoprofen and naproxen, acetylsalicylic acid presented poor recovery results, which needs to be improved.

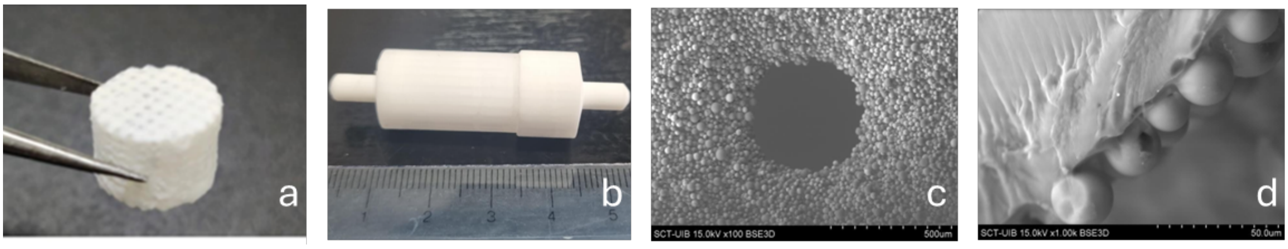

Figure 1. a) 3D coated device for SPE; b) 3D device for flow-based sampling; c) SEM image of coated device; d) SEM image of resin coat.

Acknowledgements

Financial support from the Spanish Ministry of Science and Innovation, Agencia Estatal de Investigación (project PID2019-107604RB-I00/MCIN/AEI/ 10.13039/501100011033) is gratefully acknowledged. Cesar Castro acknowledges the support from the Advanced Materials Research Center (CIMAV) S.C. and CONAHCYT for the allowance of a doctoral grant. The authors thank Calvià 2000 WWTP for allowing the sampling.

References

[1] J. Wilkinson, P.S. Hooda, J. Barker, S. Barton, J. Swinden, Occurrence, fate and transformation of emerging contaminants in water: An overarching review of the field, Environ. Pollut. 231 (2017) 954–970.

[2] T.G. Bean, E.A. Chadwick, M. Herrero-Villar, R. Mateo, V. Naidoo, B.A. Ratter, Do Pharmaceuticals in the Environment Pose a Risk to Wildlife?, Environ. Toxicol. Chem. 43 (2024) 595–610.

[3] S. Mompelat, A. Jaffrezic, E. Jardé, B. LeBot, Storage of natural water samples and preservation techniques for pharmaceutical quantification, Talanta 109 (2013) 31–45.

Activated Carbon from Grapefruit Peel as Sorbent Phase for Microextraction Technologies

PSD-25

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Keywords: *Activated carbon, Emerging contaminants, Grapefruit peel, Rotating disk sorptive extraction*

According to green analytical chemistry principles, using agricultural byproducts as sorbent phases is an interesting topic due to their lignocellulosic origin, as they are biodegradable and inexpensive. In this study, grapefruit peel and grapefruit peel activated carbon are proposed as sustainable sorbents for solid-phase microextraction technologies, which were used to assess the proof of concept.

Citrus peels are one of these by-products, commonly found day to day. One of the largest citruses found in Chile is grapefruit. Grapefruit (Citrus paradisi) is usually used to make juice or eat fresh [1].

In recent years, green analytical chemistry (GAC) has gained much attention in the scientific community, mainly focused on the sample preparation steps of chemical measurement processes. Different technologies based on solid-phase microextraction (SPME) offer eco-friendly and miniaturized alternatives to traditional sample preparation procedures, as they require a minimal amount of extractant phase and sample [2]. Despite this, since typical sorbent materials used in microextraction technologies are synthetic, they are not entirely environmentally friendly. Therefore, natural sorbent materials that align better with GAC principles are recommended [3].

Although grapefruit peel is a lignocellulosic material, its main drawback of as sorbent is the low surface area. However, this limitation can be overcome by transforming in activated carbon. The synthesis of activated carbon improves surface area and porosity, making it a viable solution to the limitation of low surface area.

In this work, grapefruit peel activated carbon was evaluated as sorbent phase to micro-extract bisphenol A (BPA) and triclosan (TCS) (as model analytes) from water samples using rotating disk sorptive extraction (RDSE) technique as a representative technology. Grapefruit peel activated carbon was characterized through N_2 adsorption isotherms, Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and the hydrophobicity hydrophilicity (HI) index were used for characterization of the proposed material. In addition, the synthesis of activated carbon was optimized by varying the temperatures, the activating agents, and their concentrations. Subsequently, the RDSE analytical methodology was developed, optimized, and validated through measurements of the analytes by gas chromatography-mass spectrometry (GC–MS).

It was found that activated carbon (AC) prepared at 400 °C with an impregnation ratio (raw material/activating agent ($ZnCl_2$), w/w) of 1:1.2 had better extraction efficiency than other ACs obtained at different temperatures, impregnation ratios, and activating agents (K_2CO_3). Characterization revealed several differences between natural grapefruit peel, biochar prepared at 400 °C, and selected AC since the typical functional groups of the natural starting material begin to disappear with pyrolysis and increasing the surface area and pore volume, suggesting that the main interactions between analytes and the sorbent material are pore filling and π-π stacking. By using this AC as the sorbent phase, the optimal extraction conditions in RDSE were as follows: the use of 10 mg of sorbent in the disk, 20 mL of sample volume, pH 2, 60 min of extraction time at a rotation velocity of the disk of 2000 rpm, and ethyl acetate as the elution solvent. The extracts were analyzed via gas chromatography and mass spectrometry (GC–MS). The method provided detection limits of 0.05 and 0.06 $\mu g\ L^{-1}$ and absolute recoveries of 21% and 73% for BPA and TCS, respectively. When comparing the extraction efficiency of the selected activated carbon with those provided by Oasis® HLB and C18 under the same conditions, nonsignificant differences were observed, indicating that grapefruit peel activated carbon is a suitable alternative to these commercial materials.

Acknowledgments

The authors would like to thank FONDECYT, Chile (Regular Project 1220225, Postdoctoral Project 3210084), FONDEQUIP (Project EQM170141), and ANID, Chile (National PhD scholarship 21200317 and National PhD scholarship 21230953) for financial support.

References

[1] M.F. Ramadan, M.A. Farag, Mediterranean Fruits Bio-Wastes: Chemistry, Functionality and Technological Applications, Springer International Publishing, Cham, 2022.

[2] A.A. Aly, T. Górecki, Green approaches to sample preparation based on extraction techniques, Molecules 25(7) (2020) 1719.

[3] A. Gałuszka, Z. Migaszewski, J. Namieśnik, The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices, TrAC Trends Anal. Chem. 50 (2013) 78-84.

Development of a Fluidic Platform for Easy Monitoring of Superoxide Anions

PSD-26

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Keywords: *Chemiluminescence, MCL, Superoxide anion*

Superoxide (O_2^-) anion is classified as a reactive oxygen species (ROS), and is involved as an oxidizing/reducing agent and initiator in multiple reactions in environmental and biological settings. However, the knowledge about its biological production is not well known. Due to the short lifetime of the superoxide anion, the use of highly sensitive and fast chemiluminogenic reactions is mandatory for its reliable quantification. In fact, luminol is widely used as a chemiluminiscence reagent but it is not selective for the superoxide ion. In this work we evaluate other reagents as lucigenin and the so-called MCLA (2-methyl-6-(4-methoxyphenyl)-3,7-dihydroimidazo[1,2-a]pyrazin-3-one hydrochloride) which have demonstrated high selectivity for superoxide in environmental waters. The MCLA probe seems to be 40-fold more sensitive for $O^{2.-}$ detection than lucigenin [1]. Therefore, in this work, we have designed a fluidic platform based on multisyringe flow injection analysis (MSFIA) for continuous forward-flow pumping of minute, well-defined volumes of samples and reagents and evaluated lucigenin and MCLA as a chemiluminescence probes. We have also evaluated the suitability of a 3D-printed flow cell directly attached to the phototomultiplier to enhance the sensitivity of the chemiluminescence system [2]. Moreover, one of the main issues for accurate quantification of superoxide derives from its instability in aqueous media that prevents obtaining reliable calibration curves from transient readouts. In this work, we have evaluated distinct non-protic organic solvents for the stabilization of the target species and found that reliable calibration plots can be obtained by preparing standards in dimethylsulfoxide. A colorimetric XTT (sodium3´-[1-(phenylaminocarbonyl)-3,4-tetrazolium]-bis(4-methoxy-6nitro)benzenesulfonicacidhydrate) assay is done to evaluate the exact concentration of the initial superoxide anion.The same assay was used to conduct a kinetic study to determine the decrease of stock solution concentration over time**.**

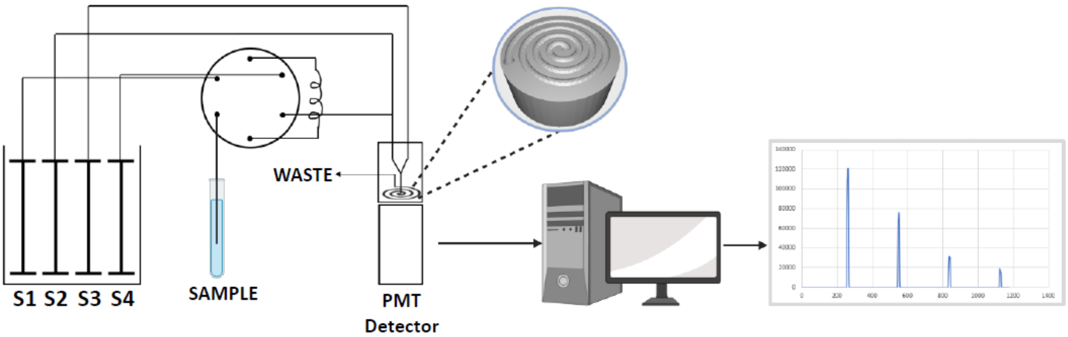

Figure 1. Flow manifold for the chemiluminescence detection of superoxide anion. Syringe 1 (S1) aspirates the sample to fill up the sample loop. S2 is filled with water, acting as a make-up flow. S3 is filled with the chemiluminescent reagent and S4 is filled with water that acts as the carrier.

Acknowledgements

The authors acknowledge financial support from the Spanish State Research Agency (Agencia Estatal de Investigacion, AEI/10.13039/501100011033), the Spanish Ministry of Science and Innovation (Ministerio de Ciencia e Innovación, MCIN), and the European Union (NextGenerationEU/PRTR) throughh projects PID2020-117686RB-C33 (AEI/MCIN) and TED2021-131303B-I00 (MCIN/AEI/NextGenerationEU/PRTR). L.G.-M. is grateful to MCIN for funding an FPI-PhD fellowship (PRE2021-100217). The authors extend their appreciation to MCIN for granting the Spanish Network of Excellence on Sustainable sample preparation (RED2022-134079-T). M.O.-R. is grateful to the Spanish Ministry of Universities and European Union (NextGenerationEU) for granting a “Margarita Salas” postdoctoral position in the framework of the Recovery, Transformation and Resilience Plan. This article is based on research from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society (DAC-EuChemS).

References

[1] S.Yamaguchi, N. Kishikawa, K. Ohyama, Y. Ohba, M. Kohno, T. Masuda, et al., Evaluation of chemiluminescence reagents for selective detection of reactive oxygen species, Anal Chim Acta 665 (2010) 74-78.

[2] L. García-Moll, A. Sixto, E.J. Carrasco-Correa, M. Miró, 3D-printed chemiluminescence flow cells with customized cross-section geometry for enhanced analytical performance, Talanta 255 (2023) 124211.

Extraction of Terbinafine from Poly(lactic-co-glycolic Acid) Based Solid Dispersions Prior to Its Determination by Fast, Sensitive UHPLC-DAD Method

PSD-27

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Keywords: *Drug delivery system, Impurities determination, Poly(lactic-co-glycolic acid), Solid dispersion, Terbinafine, UHPLC chromatography*

Our work focused on the development, optimization, and validation of the ultra-high performance chromatography (UHPLC) method, and its subsequent application in the evaluation of new drug forms based on solid dispersions serving as a delivery system for terbinafine with the intention of affecting both its release and increasing its bioavailability. We have developed a novel UHPLC method with tandem UV detection that allows fast, sensitive, and robust analysis of the antifungal drug terbinafine and its three main impurities β-terbinafine, (Z)-terbinafine, and 4-methylterbinafine in only 4.5 min [1]. This method is important in pharmaceutical analysis because it allows the detection of its impurities at very low concentrations [2]. We tested the differences between two poly(lactic-co-glycolic acid) based polymers [3].The solid dispersions were dissolved in basket apparatus. This solution was then only filtered before the analysis making the whole process even faster. The separation of the target analytes was carried out at 25 °C using a biphenyl 100 Å, 50 × 2.1 mm column packed with 1.7 µm core-shell particles. We used the less common flow rate gradient elution with the isocratic mobile phase consisting of 0.01 mol/L citrate with 0.02 mol/L phosphate buffers in a 1:1 ratio and methanol. Our results are expected to lead to the development of a new drug delivery system for topically applied terbinafine that could facilitate its administration and improve patient compliance.

Acknowledgements
This work was supported by project SVV 260 662.

References

[1] L. Kujovska Krcmova, B. Melichar, F. Svec, Analysis of terbinafine in poly(lactic-co-glycolic acid) based solid dispersions by fast sensitive UHPLC-DAD method, Anal. Methods 15 (23) 2823-2832.
[2] L. Matysova, P. Solich., P. Marek, L. Havlikova, L. Novakova, J. Sicha, Separation and determination of terbinafine and its four impurities of similar structure using simple RP-HPLC method, Talanta 68 (2006) 713–720.
[3] J. Martiska, E. Snejdrova, M. Drastik, L. Matysova, M. Dittrich, J. Loskot, P. Jilek, Terbinafine-loaded branched PLGA-based cationic nanoparticles with modifiable properties, Pharm. Dev. Technol. 24 (2019) 1308–1316.

Development of Novel Adsorbents for Extraction and Analysis of Lithium from Reverse Osmosis Brine

PSD-28

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Keywords: *Adsorbents, Recovery of Lithium, Reverse osmosis brine*

With the increasing demand for lithium worldwide, methods to obtain lithium from seawater and seawater reverse osmosis brine are being developed and researched on. In this paper, novel adsorbent materials were synthesised by combining materials such as lithium manganese oxide (LMO) spinel and lithium-ion imprinted polymers (IIP). TiO_2/PVDF membranes were selected as a support for the adsorption material. Membranes were synthesised with polymers and tested with different lithium sources. The adsorbent materials were characterised using scanning electron microscopy, energy dispersive spectroscopy, Fourier-transform infrared spectroscopy and X-ray diffraction. Characterisation methods conducted supports that the intended adsorption materials (IIP-LMO membranes) were successfully synthesised. The adsorption capacities of the IIP-LMO membranes were studied. The highest adsorption capacity calculated using IIP-LMO membranes was 4.268 mg/g. The selectivity of the IIP-LMO membranes for Li^+/Na^+ and Li^+/K^+ was also studied. The separation factors were found to be 1.061 and 0.866 respectively. With the initial adsorption tests done, there is some potential for the novel adsorption materials to have improved selectivity and efficiency, which will be useful in sample preparation for green and sustainable analytical chemistry.

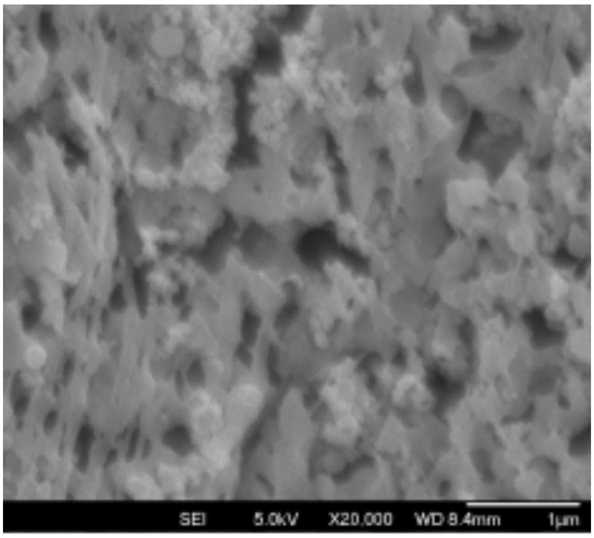

Figure 1. Scanning electron micrograph of IIP-LMO membrane.


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