EuChemS-DAC
Sample Preparation
Study Group and Network

Online event • March 11-12, 2021

1st European Sample Preparation e-Conference

Organized by the EuChemS-DAC Sample Preparation Study Group and Network

BOOK OF ABSTRACTS

EuChemS
European Chemical Society

EuChemS-DAC
Sample Preparation
Study Group and Network

1st European Sample Preparation e-Conference

Book of Abstracts

March 11-12, 2021

Title
Book of Abstracts - 1st European Sample Preparation e-Conference

Editor
EuChemS

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Date
March 2021

1st European Sample Preparation e-Conference | 11-12 March, 2021

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Welcome

Dear participants of the 1st European Sample Preparation e-Conference,

On behalf of the Organizing Committee of the EuChemS-DAC Sample Preparation Study Group and Network, it is our distinct pleasure to cordially welcome you to the 1st European Sample Preparation Conference from 11 - 12 March, 2021.

This year, due to pandemic, virtual platform is the international meeting place for chemists from all over Europe and overseas, from academic and industrial backgrounds. With key theme **"Green Sample Preparation",** this European Conference will present contributions from new technologies, and extraction techniques, addressing theory, methods or applications and highlights of new prospects and developments of current importance in analytical extraction and sample pretreatment.

Thanks to your valuable submissions, the scientific programme provides a good overview of the latest research in the area of green sample preparation.

The online programme will include access to presentations of plenary speakers, oral communications and e-posters. The best oral communication and four e-posters will be selected by an international jury and awarded for their outstanding research, thanks to support from our sponsors.

One attractive satellite event, on preparation of manuscripts, will be also organized during the conference.

We wish all attendees of 1st European Sample Preparation e-Conference an intellectually rewarding meeting providing new insights and many creative ideas for the future to come. Do not miss this excellent opportunity to share some enthusiasm in exchanging experience and ideas!

Slavica Ražić

Elia Psillakis

Chairpersons of the 1st European Sample Preparation e-Conference

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01. General information

Webex Meetings will be the e-platform used for this web conference. You may download the application here: https://www.webex.com/downloads.html

If you already have Webex installed on your computer/mobile, it is strongly recommended to download and install the latest Webex upgrades before joining the meeting, in particular, to participate in the Breakout sessions. Failing to do that might not permit you to join the Webex meeting and Breakout Sessions.

General instructions on how to use Webex and joining a meeting can be found at the Cisco Webex Help Center.

The general instructions to Get Started with Cisco Webex Meetings for Attendees can be found here.

Follow this short tutorial to get familiarized with the e-platform.

If there are any questions, please contact:
Assoc. Prof. Cecilia Cagliero at cecilia.cagliero@unito.it

During the event if there are any technical problems or requests you may contact:
cecilia.cagliero@unito.it
or
sampleprep@enveng.tuc.gr

Please note, that all participants are requested to **connect at least 10 min** before session/talks to ensure sufficient time for admission in the event.

Conference link

Only registered participants will have access to this Webex event.

The Webex link to the meeting is:
https://unito.webex.com/unito-en/j.php?MTID=m2a3b7e35236c7f44283b5eb74b437b91
Meeting number: 121 344 4894
Meeting password: 8zyYi7YdQw3

Instructions for the audience of oral presentations

- The microphones of the audience will be muted during oral presentations.
- It is recommended that you inactivate your camera during oral presentations.
- After each talk and depending on the time left, the chairs of each session will decide if there is time left for questions to be asked in public. In this case, the microphones will be unmuted and you may use your camera if you wish. **If you wish to ask a question please "raise your hand"** and wait for one of the session chairs to unmute you (see image below).

- If there is no time left for questions you may (i) use Chat to reach the speaker privately or (ii) ask the Chairs to create a Breakout session for discussing with the speaker the results presented.

Instructions for oral presenters

- Few minutes before the scheduled time of your presentation you will be notified by the Session Chair in a private message that your talk is next.
- You will be permitted to use your microphone and Share your Screen during your oral presentation. Please press share and choose the window of your PowerPoint or PDF file to initiate your presentation (see image below). More information on how to share can be found **here**.

Instructions for poster presenters and the audience

All posters will be stored in this **Google drive**

During each Poster Session, two separate Breakout Sessions will be created. Please, see at this link the Best Practices for Participating in Breakout Sessions.
Please, note that the Breakout sessions are available only on the Cisco Webex Meetings Desktop App on WBS40.9 and later sites.

- The Attendees can choose which Breakout Session they prefer to join and open poster files stored in Google Drive.
- The Poster Presenters **have to join** their assigned session.
- The Poster Presenters will have two minutes to present their poster.

Questions in the Breakout Sessions can be asked only using the Chat.

- Use Chat to address your question to the Chairs for the general broadcast of your question.
- Request the Chairs to create a Breakout Session for discussing with the poster presenter the results/conclusion.

Please note that at any time (i) you can use the Chat to interact with other participants and (ii) ask the Chairs to create a Breakout Session for you to interact with other participants

Interdisciplinary plenary lectures

“Green Sample Preparation" is the key theme of the 1st European Sample Preparation e-Conference and interdisciplinary plenary lectures in Green Chemistry will be presented during the conference:

Paul T. Anastas, professor at Yale University, School of the Environment, USA, will present a plenary lecture entitled: **"The Periodic Table of the Elements of Green and Sustainable Chemistry".** Professor Paul T. Anastas is credited with establishing the field of green chemistry in 1991 during his time working for the U.S. Environmental Protection Agency as the Chief of the Industrial Chemistry Branch and as the founding Director of the U.S. Green Chemistry Program. Dr. Anastas has published widely on topics of science through sustainability.

Dr. Vania Zuin, professor at the Federal University of São Carlos (Brazil), will present a plenary lecture on Green Chemistry entitled: ***"To prepare or not to prepare samples: what is necessary for a green and sustainable extraction of bioactive compounds from agro-industrial wastes".***

Dr. Nora Ventosa, scientific researcher of the Institute of Materials Science of Barcelona (ICMAB) of CSIC and delegate at the EuChemS Division of Green and Sustainable Chemistry, will present a lecture on the activities and mission of the EuChemS Division of Green and Sustainable Chemistry next to the activities of her team. The lecture is entitled: ***"EuChemS Division of Green and Sustainable Chemistry/Compressed CO_2: an attractive green solvent for the preparation of nanostructured materials".***

Satellite event

During the 1st European Sample Preparation e-Conference, a Satellite Event will deal with the preparation of manuscripts. Contributors are:

Prof. František Švec giving a lecture entitled: “Preparation of manuscript that is likely to be accepted in high end journal” and

Prof. Manuel Miró giving a short-lecture entitled: “How to write a scientifically sound review article-Tips and tricks"

Oral and poster awards

We are pleased to announce you that one Oral and four Poster Awards will be granted to the best contributions presented by young scientists at the 1st European Sample Preparation e-Conference as follows:

Best Oral Communication Award: 400 €. Sponsored by **LECO**.

Best Poster Award: Automation in sample preparation: 250 €. Sponsored by **AXEL-SEMRAU**.

Best Poster Award: 250 €. Sponsored by **LECO**.

Best Poster Award: 250 €. Sponsored by **SHIMADZU**.

Best Poster Award: 250 €. EuChemS-Dac Sample Preparation Study Group and Network.

The selection of winners will be carried out by our scientific committee based on excellence criteria.

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EuChemS

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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.

Through the promotion of chemistry and by providing expert and scientific advice, EuChemS aims to take part of the solution to today´s major societal challenges.

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

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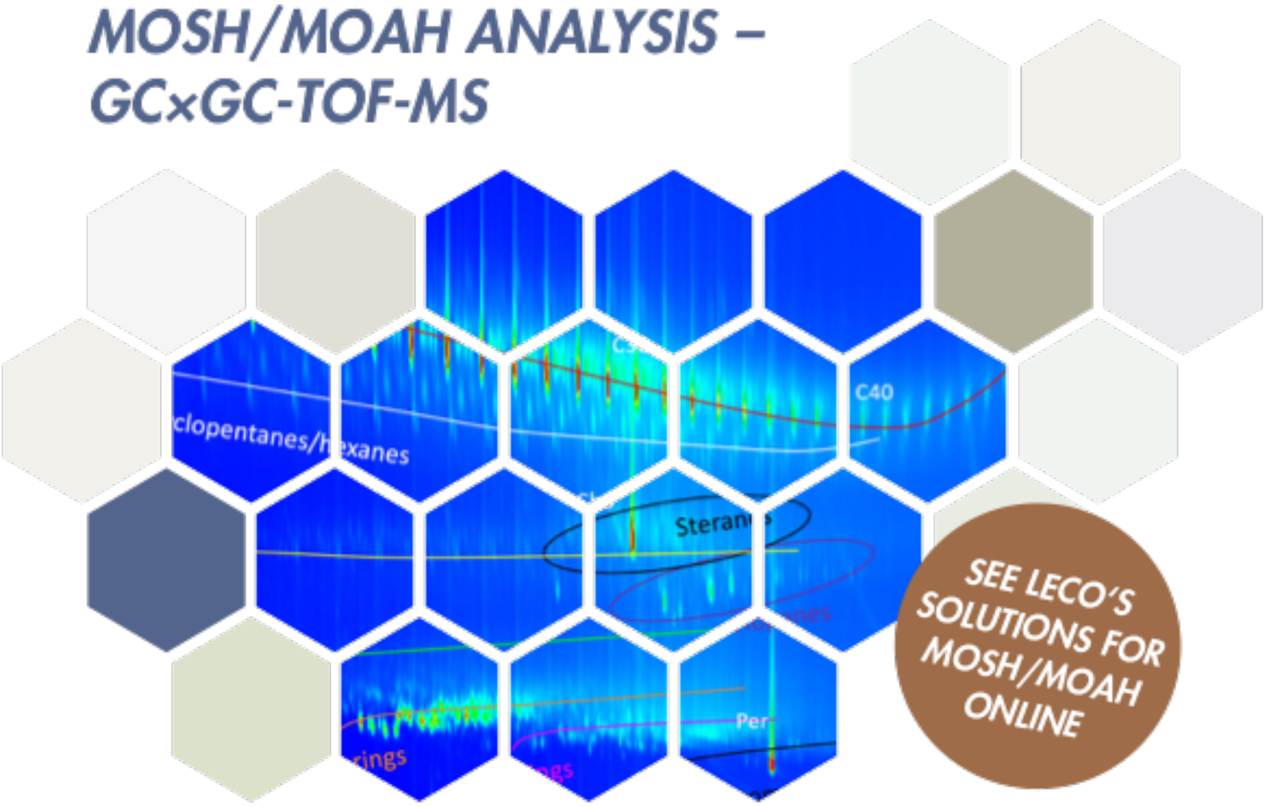

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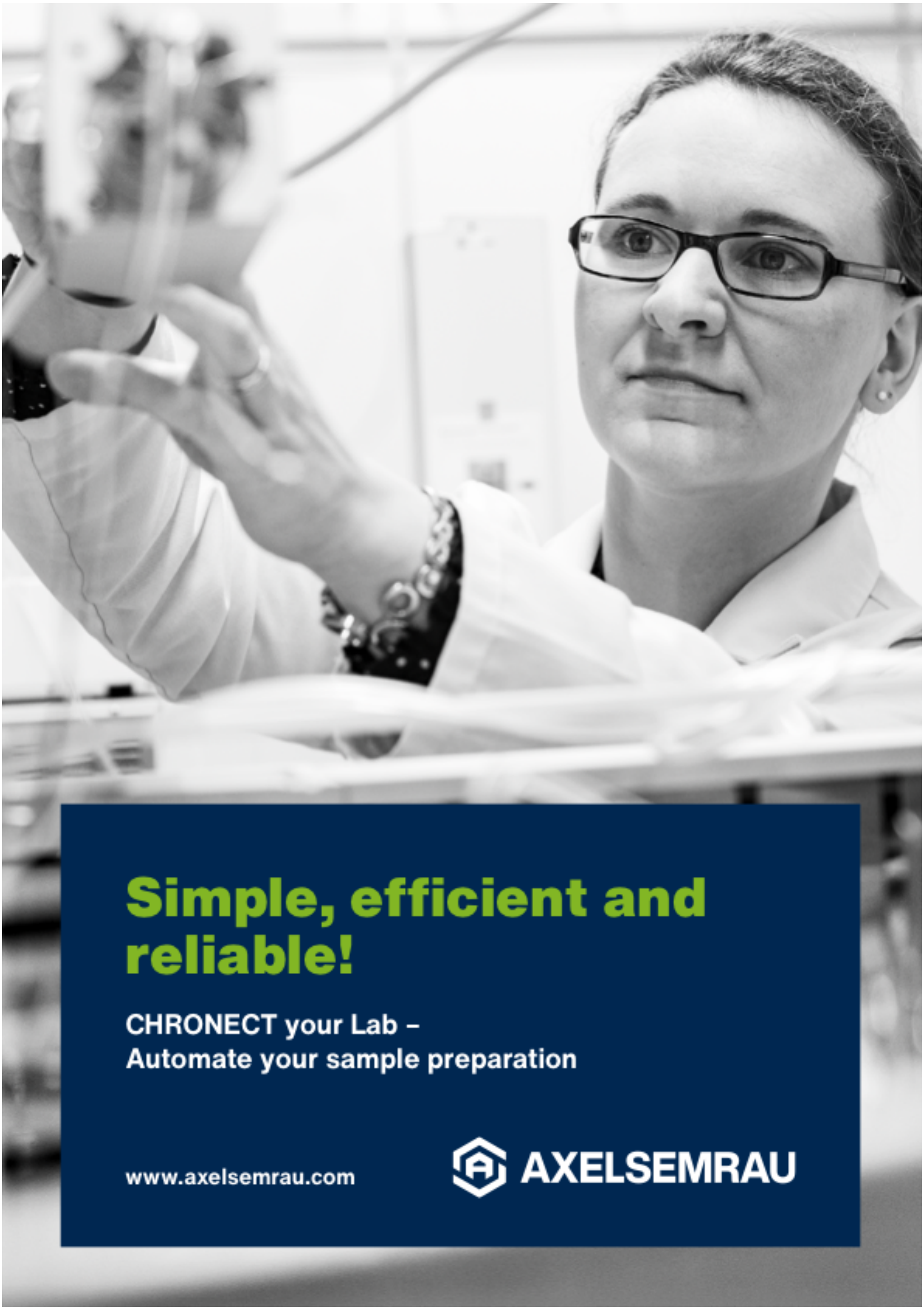

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23rd International Symposium on Advances in Extraction Technologies

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https://extech2021.com

We are pleased to announce the **23rd edition of ExTech**, the International Symposium on Advances in Extraction Technologies, to be held at the University of Alicante (Spain) in 2021.

The **ExTech symposium** series is the flagship event for sample preparation, analytical extraction processes, and sample clean-up techniques. The series, started in 1999 by Prof. Janusz Pawliszyn (Canada), has been held annually around the world. **ExTech** has become a unique and vital platform for the exchange of information and ideas in the growing field of sample preparation. The Symposium is focused on the fundamentals, developments, and new technologies of extraction and sample preparation in different areas of analytical sciences including new extraction phases and technologies, remote sensing, in-vivo analysis, microfluidics, lab-on-a-chip, diagnostic tool, etc.

During the symposium plenary, keynotes and oral lectures, poster presentations, workshops and industrial exhibition will be scheduled. Contributions to ExTech2021 will be published in a special issue of Analytica Chimica Acta, Talanta and JCA.

IMPORTANT DATES

Call for abstracts	11th January 2021
~~Deadline for submission of abstracts~~	~~11th March 2021~~
Extended deadline for submision of abstracts	11th April 2021

Contact: **extech2021@transviabusiness.com**

Looking forward to seeing you in Alicante in June 2021!

Lorena Vidal & Manuel Miró
Chair and Cochair ExTech2021
Janusz Pawliszyn
Honorary Chair

03. Participants map

04. Scientific Programme at a glance

Please mind that the **detailed programme is scheduled for CET** (Belgium, Croatia, Czech Republic, Denmark, France, Germany, Italy, Norway, Poland, Serbia, Slovenia, Spain, and Switzerland). The schedule for **GMT** (Portugal, and the UK) and **EET** (Cyprus and Greece) is also indicated here. For Turkey **EET+1h** should be applied. Non-European participants are advised to calculate their local time by using the GMT.

CET	Thursday, 11 March 2021	GMT	EET	CET	Friday, 12 March 2021	GMT	EET
09:00	Opening Session	08:00	10:00	09:00	Oral Session-O5	08:00	10:00
09:10	Plenary Lecture	08:10	10:10				
09:30	Oral Session-O1	08:30	10:30				
10:30	Break	09:30	11:30	10:30	Break	09:30	11:30
11:00	Oral Session-O2	10:00	12:00	11:00	Oral Session-O6	10:00	12:00
12:00	Satellite Event	11:00	13:00	12:00	Round Table Discussion	11:00	13:00
13:00	Poster Sessions A & B	12:00	14:00	13:00	Poster Sessions C & D	12:00	14:00
14:00	Oral Session-O3	13:00	15:00	14:00	Oral Session-O7	13:00	15:00
15:15	Break	14:15	16:15				
15:30	Oral Session-O4: Young Scientists	14:30	16:30	15:30	Break	14:30	16:30
				15:45	Oral Session-O8	14:45	16:45
				16:30	Plenary Lecture	15:30	17:30
				16:50	Plenary Lecture	15:50	17:50
17:10	One-to-one meetings	16:10	18:10	17:10	Closing Session/Awards	16:10	18:10
17:30		16:30	18:30	17:30		16:30	18:30

05. Scientific Programme – detailed schedule

The programme schedule is given in CET

	Thursday, 11 March 2021
9:00 - 9:10	**Opening Session:** **S. Ražić,** Chair of EuChemS-DAC, University of Belgrade, Serbia **E. Psillakis,** Head of EuChemS-DAC Sample Preparation Study Group and Network, Technical University of Crete, Greece
Oral Session O1	**Chairs: S. Ražić, E. Psillakis**
9:10 - 9:30	**PL1. To Prepare or not to Prepare Samples: What is Necessary for a Green and Sustainable Extraction of Bioactive Compounds from Agro-industrial Wastes** **V.G. Zuin[1-3].** *(1) Department of Chemistry, Federal University of São Carlos, Rod. Washington Luís (SP-310), km 235, 13565-905, São Carlos, SP, Brazil.* *(2) Institute of Sustainable and Environmental Chemistry, Leuphana University, Universitätsallee 1, 21335, Lüneburg, Germany.* *(3) Green Chemistry Centre of Excellence, University of York, Heslington, York, YO10 5DD, UK.*
9:30 - 9:45	**O-1. Electromembrane Extraction – Sample Preparation Based on Electrokinetic Extraction Across a Supported Liquid Membrane** **S. Pedersen-Bjergaard[1,2].** *(1) Department of Pharmacy, University of Oslo, P.O. Box 1068 Blindern, 0316 Oslo, Norway.* *(2) Department of Pharmacy, Faculty of Health and Medical Sciences, University of Copenhagen, Universitetsparken 2, 2100 Copenhagen, Denmark.*
9:45 - 10:00	**O-2. Ionic Liquids: An "Old" Class of Chemicals of High Interest in Modern Sample Preparation and Analysis** **C. Bicchi**, C. Cagliero. *Laboratory of Pharmaceutical Biology and Food Chemistry. Dipartimento di Scienza e Tecnologia del Farmaco, Università di Torino, Torino, Italy.*
10:00 - 10:15	**O-3. In Situ Growth of Imidazolium-based Porous Organic Polymer via Controlled Polymerization in Confined Space for In Vivo Microextraction** **G. Ouyang**[1], Q. Hu[1], H. Fang[2], J. Huang[1], X. Liu[1], J. Xu[2], J. Zhang[2]. *(1) KLGHEI of Environment and Energy Chemistry, School of Chemistry, Sun Yat-sen University, Guangzhou, Guangdong 510275, China.* *(2) MOE Laboratory of Polymeric Composite and Functional Materials, School of Materials Science and Engineering, Sun Yat-sen University, Guangzhou 510275, China.*
10:15 - 10:30	**O-4. Bead Injection as In-Line Renewable Solid-Phase Extraction Approach: Is There Room for Improvement?** **M. Miró.** *FI-TRACE Group, Department of Chemistry, University of Balearic Islands, Carretera de Valldemossa, Km 7.5, E 07122, Palma de Mallorca, Spain.*

10:30 - 11:00	**Coffee Break**

Oral Session O2 **Chairs: M. Segundo, S. Pedersen-Bjergaard**

11:00 - 11:15 **O-5. Sustainable Supports for Microextraction**

R. Lucena, S. Cárdenas.

Departamento de Química Analítica, Instituto Universitario de Investigación en Química Fina y Nanoquímica (IUNAN), Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie, E-14071 Córdoba, Spain.

11:15 - 11:30 **O-6. Mixed-mode Amphoteric Materials to Solid-Phase Extract Ionisable Compounds from Environmental Waters**

N. Fontanals[1], J.C. Nadal[1], F. Borrull[1], P.A.G. Cormack[2], R.M. Marcé[1].

(1) Department of Analytical Chemistry and Organic Chemistry, Universitat Rovira i Virgili, Sescelades Campus, Marcel·lí Domingo 1, 43007 Tarragona, Spain.

(2) WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow, G1 1XL, Scotland, United Kingdom.

11:30 - 11:45 **O-7. An Innovative Green Protocol for the Quantification of Benzothiazoles, Benzotriazoles and Benzenesulfonamide in PM10 Using Microwave-Assisted Extraction Coupled with Solid-Phase Microextraction Gas Chromatography Tandem-Mass Spectrometry**

A. Naccarato[1], A. Tassone[1], M. Martino[1], R. Elliani[2], F. Sprovieri[1], N. Pirrone[1], A. Tagarelli[2].

(1) CNR-Institute of Atmospheric Pollution Research, c/o UNICAL polifunzionale – 87040 Rende (CS), Italy.

(2) Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria – 87040 Rende (CS), Italy.

11:45 - 12:00 **O-8. Combining Headspace Microextraction Approaches with Miniaturized Detection Systems and IT Equipment for Determination of Anionic Species**

F. Pena-Pereira, I. Lavilla, C. Bendicho.

Centro de Investigación Mariña, Universidade de Vigo, Departamento de Química Analítica e Alimentaria, Grupo QA2, 36310 Vigo, España.

Satellite Event: The art of scientific publication

Chair: S.A. Ozkan

12:00 - 12:30 **Preparation of Manuscript That is Likely to be Accepted in High End Journal**

F. Švec

Faculty of Pharmacy in Hradec Kralove, Charles University, Prague, Czech Republic

12:30 – 12:40 **Q&A**

12:40 – 12:50 **How to Write a Scientifically Sound Review Article-Tips and Tricks**

M. Miró.

FI-TRACE Group, Department of Chemistry, University of Balearic Islands, Carretera de Valldemossa, Km 7.5, E 07122, Palma de Mallorca, Spain

12:50 – 13:00 **Q&A**

Poster Session A **Chairs: S. Ražić, M. Zoccali**

13:00 - 14:00 **Parallel poster session Break Room PS-A**

Poster Session B **Chairs: R. Lucena, G. Purcaro**

13:00 - 14:00 **Parallel poster session Break Room PS-B**

Oral Session O3 — Chairs: S.A. Ozkan, F. Pena-Pereira

14:00 - 14:15

O-9. Ionic Liquids for Micro-Scale Extractions from Plants: From the Plant Genome to the Plant Metabolome

C. Cagliero[1], A. Marengo[1], G. Mastellone[1], B. Sgorbini[1], C. Bicchi[1], V. Pino[2], J. Anderson[3], P. Rubiolo[1].

(1) Dipartimento di Scienza e Tecnologia del Farmaco, Università degli Studi di Torino, I-10125 Torino, Italy.
(2) Laboratorio de Materiales para Análisis Químicos (MAT4LL), Departamento de Química, Unidad Departamental de Química Analítica, Universidad de La Laguna (ULL), 38206 Tenerife, Spain.
(3) Ames Laboratory—USDOE and Department of Chemistry, Iowa State University, Ames, IA 50011, USA.

14:15 - 14:30

O-10. Task Specific Ionic Liquids Based on 2-mercaptobenzothiazole for Selective Extraction of Cd

T. Trtić-Petrović[1], I. Pušica[1], S. Ražić[2], M. Vraneš[3], S. Papović[3], S. Gadžurić[3].

(1) University of Belgrade, Vinča Institute of Nuclear Sciences, National Institute of the Republic of Serbia, P.O.Box 522, 11001 Belgrade, Serbia.
(2) University of Belgrade, Faculty of Pharmacy - Department of Analytical Chemistry, Belgrade, Serbia.
(3) University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovića3, 21000 Novi Sad, Serbia.

14:30 - 14:45

O-11. Modeling the Effect of Temperature on Solid-Phase Microextraction of Volatile Organic Compounds from Air Using Finite Element Analysis

B. Kenessov, D. Orazbayeva, N.V. Bakaikina, A. Kapar, A. Muratuly, B. Bukenov.

Center of Physical Chemical Methods of Research and Analysis, Al-Farabi Kazakh National University, 96A Tole bi street, Almaty, 050012, Kazakhstan.

14:45 - 15:00

O-12. The Impact of Solid Phase Microextraction (SPME) Adsorbent Properties on Analytical Performance

D. Mendivelso[1], O. Shimelis[1], S. Shollenberger[1], F. Michel[2], K. Buckendahl[1].

(1) MilliporeSigma, 595 N. Harrison Road, Bellefonte, PA 16823 USA.
(2) Sigma-Aldrich Chemie GmbH, Eschenstraße 5, 82024 Taufkirchen, Germany.

15:00 - 15:15

O-13. Asking Better Questions in Microextraction

E. Psillakis.

Laboratory of Aquatic Chemistry, School of Environmental Engineering, Technical University of Crete, GR-73100, Chania, Crete, Greece.

15:15 - 15:30

Coffee Break

Oral Session O4 — OS Young Scientists

Chairs: E. Psillakis, R. Lucena

15:30 - 15:40

O-14. Microfluidic Paper-Based Analytical Devices for Sample Preparation and Rapid Detection

Y. Pan[1,2], Z. Yang[2].

(1) School of Engineering, University of Glasgow, Glasgow, G12 8LT, UK.
(2) Cranfield Water Science Institute, Cranfield University, Bedfords, MK43 0AL, UK.

15:40 - 15:50

O-15. Miniaturized Active Air Sampling Method for the Analysis of Tire Rubber Pollutants from Indoor and Outdoor Places

D. Armada[1], M. Celeiro[1], A. Martínez-Fernández[1], P. Nurerk[1, 2], T. Dagnac[3], M. Llompart[1].

(1) CRETUS Institute, Department of Analytical Chemistry, Nutrition and Food Science, Universidade de Santiago de Compostela, E-15782, Santiago de Compostela, Spain.
(2) Functional Materials and Nanotechnology Center of Excellence, School of Science, Walailak University, Nakhon Si Thammarat 80160, Thailand.
(3) Agronomic and Agrarian Research Centre (AGACAL-CIAM), Galician Agency for Food Quality, Unit of Organic Contaminants, Apartado 10, E-15080, A Coruña. Spain.

15:50 - 16:00 O-16. Column Switching for Automated Online Enrichment and Separation of Polar and Nonpolar Analytes from Aqueous Matrices

K. Kochale[1,2], T. Teutenberg[1], T.C. Schmidt[2].

(1) Institut für Energie- und Umwelttechnik e.V., Bliersheimer Strasse 58-60, 47229 Duisburg.
(2) University Duisburg-Essen, Universitaetsstrasse 5, 45141 Essen.

16:00 - 16:10 O-17. Chromatographic Fingerprinting and Accurate Quantitative Profiling by Multiple Headspace Solid Phase Microextraction and Differential-Flow Modulated Comprehensive Two-Dimensional Gas Chromatography: The Aroma Blueprint of Extra Virgin Olive Oil

F. Stilo[1], C. Bicchi[1], S. E. Reichenbach[2,3], J. McCurry[4], D. Peroni[5], C. Cordero[1].

(1) Institut für (1) University of Turin, Dipartimento di Scienza e Tecnologia del Farmaco - Via Pietro Giuria 9, 10125, Torino, Italy.
(2) Computer Science and Engineering Department, University of Nebraska,256 Avery Hall, Lincoln, NE 68588, USA
(3) GC Image LLC – 201 N 8th St Unit 420, Lincoln, NE 68508, USA
(4) Agilent Technologies, Gas Phase Separations Division – 2850 Centerville Rd, Wilmington, DE 19808, USA
(5) SRA Intruments SpA – Via alla Castellana 3, 20063, Cernusco sul Naviglio, Italy

16:10 - 16:20 O-18. Working Towards Comprehensive Steroid Detection in Urine via Targeted MIPs Clean-up and Fully Automated GCxGC-MS Analysis.

R. A. Hand[1,2], G. Morgan[2], T. Bassindale[3], N. Turner[1].

(1) School of Pharmacy, De Montfort University, Leicester, LE2 9BH, UK.
(2) School of Physical Sciences, The Open University, Milton Keynes, MK7 6AA, UK.
(3) Department of Biosciences and Chemistry, Sheffield Hallam University, Sheffield, S1 1WB, UK.

16:20 - 16:30 O-19. Lab-In-Syringe Automated Double-Stage Extraction for the Determination of Sulfonamides Antibiotics in Urine

K. Fikarová, B. Horstkotte, D. Machián, H. Sklenářová, P. Solich.

Charles University, Faculty of Pharmacy in Hradec Králové, Department of Analytical Chemistry, Akademika Heyrovského 1203, 500 05 Hradec Králové, Czech Republic.

16:30 - 16:40 O-20. Fabric Phase Sorptive Extraction Followed by Gas Chromatography-Tandem Mass Spectrometry for the Analysis of Multiclass Fungicides in Water

L. Vázquez[1], M. Celeiro[1], T. Dagnac[2], A. Kabir[3], M. Llompart[1].

(1) CRETUS Institute, Department of Analytical Chemistry, Nutrition and Food Science, Faculty of Chemistry, Universidade de Santiago de Compostela, E-15782, Santiago de Compostela, Spain.
(2) Agronomic and Agrarian Centre (AGACAL-CIAM), Unit of Organic Contaminants, Apartado 10, E-15080, A Coruña, Spain.
(3) International Forensic Research Institute, Department of Chemistry and Biochemistry, Florida International University, Miami, FL-33199, USA.

16:40 - 16:50 O-21. Menthol-Based Deep Eutectic Solvent Dispersive Liquid-Liquid Microextraction: A Simple and Quick Approach for the Analysis Extraction of Phthalic Acid Esters from Water, Beverages and Infusions

J. González-Sálamo[1,2], C. Ortega-Zamora[1], G. Jiménez-Skrzypek[1], C. Hernández-Sánchez[2,3], J. Hernández-Borges[1,2].

(1) Universidad de La Laguna, Departamento de Química, Unidad Departamental de Química Analítica, Facultad de Ciencias, Avda. Astrofísico Fco. Sánchez, s/n°. 38206 San Cristóbal de La Laguna, Spain.
(2) Universidad de La Laguna, Instituto Universitario de Enfermedades Tropicales y Salud Pública de Canarias, Avda. Astrofísico Fco. Sánchez, s/n°. 38206 San Cristóbal de La Laguna, Spain.(3) Universidad de La Laguna, Departamento de Obstetricia y Ginecología, Pediatría, Medicina Preventiva y Salud Pública, Toxicología, Medicina Forense y Legal y Parasitología, Área de Medicina Preventiva y Salud Pública, Escuela Politécnica Superior de Ingeniería, Sección de Náutica, Máquinas y Radioelectrónica Naval, Vía Auxiliar Paso Alto, n° 2. 38001 Santa Cruz de Tenerife, Spain.

16:50 - 17:00 O-22. Fabric Phase Sorptive Extraction: A Convenient Tool for Therapeutic Drug Monitoring, Illicit Drug Investigation and Other Clinical/Toxicological Study Using Unconventional Biological Fluids

A. Tartaglia[1], A. Kabir[2], H.I. Ulusoy[3], G.M. Merone[4], F. Savini[5], C. D'Ovidio[6], E. Rosato[1], U. De Grazia[7], K.G. Furton[2], M. Locatelli[1].

(1) Department of Pharmacy, University of Chieti–Pescara "G. d'Annunzio", Via dei Vestini 31, Chieti 66100, Italy.
(2) Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th St, Miami, FL 33199, USA.
(3) Department of Analytical Chemistry, Faculty of Pharmacy, Cumhuriyet University, Sivas 58140, Turkey.
(4) Department of Neuroscience, Imaging and Clinical Sciences, University of Chieti–Pescara "G. d'Annunzio", 66100 Chieti, Italy.
(5) Pharmatoxicology Laboratory—Hospital "Santo Spirito", Via Fonte Romana 8, Pescara 65124, Italy.

(6) Department of Medicine and Aging Sciences, Section of Legal Medicine, University of Chieti–Pescara "G. d'Annunzio", Chieti 66100, Italy.
(7) Fondazione IRCCS Istituto Neurologico Carlo Besta, Laboratory of Neurological Biochemistry and Neuropharmacology, Via Celoria 11, Milan 20133, Italy.

17:00 - 17:10

O-23. Electromembrane Extraction Using Deep Eutectic Solvents As Liquid Membrane

F.A. Hansen[1], E. Santigosa-Murillo[2], M. Ramos-Payán[3], M. Muñoz[2], E. Leere Øiestad[4], S. Pedersen-Bjergaard[1,5].
(1) Department of Pharmacy, University of Oslo, P.O. Box 1068 Blindern, 0316 Oslo, Norway.
(2) Department of Analytical Chemistry, Universitat Autónoma de Barcelone, 08193 Bellaterra, Barcelona, Spain.
(3) Department of Analytical Chemistry, University of Seville, 41012 Seville, Spain.
(4) Oslo University Hospital, Division of Laboratory medicine, Department of Forensic Sciences, P.O. Box 4459 Nydalen, 0424 Oslo, Norway.
(5) School of Pharmaceutical Sciences, Faculty of Health and Medical Sciences, University of Copenhagen, Universitetsparken 2, 2100 Copenhagen, Denmark.

17:10 – 17:30

One-to-one meetings

Friday, 12 March 2021

Oral Session O5 **Chairs: S. Ražić, R. Lucena**

9:00 - 9:15 **O-24. Sample Introduction and Multidimensionality as Part of Sample Preparation**

G. Purcaro.

Gembloux Agro-Bio Tech, University of Liege, Passage des Déportés, 2, Gembloux, B-5030, Belgium.

9:15 - 9:30 **O-25. Automatization and Miniaturization of Sample Preparation of Food and Biological Samples for Lipidomics Studies**

D. Donnarumma[1], G. Micalizzi[1], F. Rigano[2], L. Mondello[1,2,3,4].

(1) Chromaleont s.r.l., Messina, Italy.
(2) University of Messina, Messina, Italy,
(3) BeSep s.r.l., Messina, Italy.
(4) University Campus Bio-Medico of Rome, Rome, Italy.

9:30 - 9:45 **O-26. Automated Analysis of 2-,3-MCPD and Glycidyl Esters in Edible Oils and Fats**

T. Cucu, C. Devos, F. David, P. Sandra.

RIC, Pres. Kennedypark 26, B-8500 Kortrijk, Belgium.

9:45 - 10:00 **O-27. Aroma Discovery of Low-cost to Luxury Honey Using a High-Capacity Sorptive Extraction Technique (HiSorb) and Gas Chromatography Mass Spectrometry**

N.D. Spadafora[1-2], R. Szafnauer[1], R. Cole[1], L. McGregor[3], N. Bukowski[1].

(1) Markes International Ltd, Gwaun Elai Medi-Science Campus, Llantrisant, RCT, CF72 8XL, UK
(2) Department of Biology, Ecology and Earth Sciences, University of Calabria, Via Ponte P. Bucci Cubo 6b, 87036, Arcavacata Di Rende, Cosenza, Italy.
(3) SepSolve Analytical Ltd, 4 Swan Court, Hampton, PE7 8GX, Peterborough, UK.

10:00 - 10:15 **O-28. Determination of 2-Methyisoborneol and Geosmin as Malodours in Catfish for Quality Control Using a Fully Automated Sample Prep Platform Coupled with Gas Chromatography and Mass Spectrometry**

R. Szafnauer[1], R. Cole[1], L. McGregor[2], N. Bukowski[1], N.D. Spadafora[1-3].

(1) Markes International Ltd, Gwaun Elai Medi-Science Campus, Llantrisant, RCT, CF72 8XL, UK.
(2) SepSolve Analytical Ltd, 4 Swan Court, Hampton, PE7 8GX, Peterborough, UK.
(3) Department of Biology, Ecology and Earth Sciences, University of Calabria, Via Ponte P. Bucci 6b, 87036, Arcavacata Di Rende, Cosenza, Italy.

10:15 - 10:30 **O-29. Development of A Low-Cost, Lab-Made Y-Interface for LC-GC Coupling for On-line Analysis in a Fully Automatized Way of Mineral Oils in Food Samples.**

M. Zoccali[1], A. Arena[1], P.Q. Tranchida[1], L. Mondello[1,2,3,4].

(1) University of Messina, Messina, Italy.
(2) Chromaleont s.r.l., Messina, Italy.
(3) BeSep s.r.l., Messina, Italy.
(4) University Campus Bio-Medico of Rome, Rome, Italy.

10:30 - 11:00 **Coffee Break**

Oral Session O6 **Chairs: M. Miró, A. Martín-Esteban**

11:00 - 11:15

O-30. 3D-printed Stirring Cages for Semi-Dispersive Fibrous Sorbent Extraction of Bisphenols

B. Horstkotte, I.H. Šrámková, D. Šatínský, P. Solich.

Charles University, Faculty of Pharmacy, Department of Analytical Chemistry, Akademika Heyrovského 1203, 5005 Hradec Králové, Czech Republic.

11:15 - 11:30

O-31. Automation of Immunoaffinity Extraction Using the Bead Injection Concept

M.A. Segundo, S.S. Marques, I.I. Ramos, L. Barreiros.

LAQV, REQUIMTE, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, R Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal.

11:30 – 11:45

O-32. Combining Lab-In-Syringe with Bead-Injection for Preconcentration of Nonsteroidal Anti-Inflammatory Drugs in Surface Waters Coupled Online to High Performance Liquid Chromatography

C.V. Gemuh, B. Horstkotte, P. Solich.

Department of Analytical Chemistry, Faculty of Pharmacy, Charles University, Akademika Heyroyskeho 1203, 500 05 Hradec Kralove, Czech Republic.

11:45 - 12:00

O-33. Automated Monitoring in Sequential Injection Analysis

H. Sklenářová[1], R. Ernest[1], B. Horstkotte[1], M. Miró[1,2], P. Solich[1].

(1) Charles University, Faculty of Pharmacy, Akademika Heyrovského 1203, 500 05 Hradec Králové, Czech Republic.

(2) FI-TRACE group, Department of Chemistry, University of the Balearic Islands, Palma de Mallorca, Spain.

12:00 - 13:00

Round Table Discussion: Green Sample Preparation

Moderators: V. Zuin, S.A. Ozkan, Á.I. López-Lorente, S. Pedersen-Bjergaard, E. Psillakis

Poster Session C **Chairs: M. Segundo, E. Psillakis**

13:00 - 14:00 **Parallel poster session Break Room PS-C**

Poster Session D **Chairs: S. Ražić, M. Zoccali**

13:00 - 14:00 **Parallel poster session Break Room PS-D**

Oral Session O7 **Chairs: G. Purcaro, F. Pena-Pereira**

14:00 - 14:15

O-34. Magnetic Dispersive Solid-Phase Extraction Using a Zeolite-Based Composite for Direct Electrochemical Determination of Lead(II) in Urine Using Screen-Printed Electrodes

L. Vidal[1], E. Fernández[1], J. Silvestre-Albero[2], A. Canals[1].

(1) Departamento de Química Analítica, Nutrición y Bromatología e Instituto Universitario de Materiales, Universidad de Alicante, E-03080 Alicante, Spain.

(2) Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica-Instituto Universitario de Materiales, Universidad de Alicante, E-03080 Alicante, Spain.

14:15 - 14:30 **O-35. Influence of Sampling Trap Materials on the Volatilome From *In Vitro* and *Ex Vivo* Samples**

F.A. Franchina, D. Zanella, T. Dejong, J.-F. Focant.

Organic and Biological Analytical Chemistry Group, MolSys, University of Liège, Belgium.

14:30 - 14:45 **O-36. Fabric Phase Sorptive Membrane Array: A Novel Approach for Non-Invasive In Vivo Sampling for Disease Diagnosis, Air Pollution monitoring, and Beyond**

M. Locatelli[1], A. Tartaglia[1], H.I. Ulusoy[2], S. Ulusoy[3], F. Savini[4], S. Rossi[4], F. Santavenere[4], G.M. Merone[5], E. Bassotti[6], C. D'Ovidio[7], E. Rosato[7], K.G. Furton[8], A. Kabir[8].

(1) Department of Pharmacy, University of Chieti–Pescara "G. d'Annunzio", Via dei Vestini 31, Chieti 66100, Italy.
(2) Department of Analytical Chemistry, Faculty of Pharmacy, Cumhuriyet University, Sivas 58140, Turkey.
(3) Department of Chemistry, Faculty of Science, Cumhuriyet University, Sivas 58140, Turkey.
(4) Pharmatoxicology Laboratory—Hospital "Santo Spirito", Via Fonte Romana 8, Pescara 65124, Italy.
(5) Department of Neuroscience, Imaging and Clinical Sciences, University of Chieti–Pescara "G. d'Annunzio", 66100 Chieti, Italy.
(6) R&D Department Eureka Lab Division, Chiaravalle, Italy.
(7) Department of Medicine and Aging Sciences, Section of Legal Medicine, University of Chieti–Pescara "G. d'Annunzio", Chieti 66100, Italy.
(8) Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th St, Miami, FL 33199, USA.

14:45 - 15:00 **O-37. Application of New HLB Solid Phase Extraction Towards Analysis of Pharmaceuticals in Plasma Samples**

F. Michel[1], M.J. Ross[2], O. Shimelis[2], C. Price[2].

(1) Sigma-Aldrich Chemie GmbH, Eschenstraße 5, 82024 Taufkirchen, Germany.
(2) MilliporeSigma, 595 N. Harrison Road, Bellefonte, PA 16823 USA.

15:00 - 15:15 **O-38. Measurement of Protein Binding Property of Drugs Using High-Throughput Automated Solid Phase Microextraction and LC-MS/MS Detection**

O. Shimelis[1], M.J. Ross[1], F. Michel[2].

(1) MilliporeSigma, 595 N. Harrison Road, Bellefonte, PA 16823 USA.
(2) Sigma-Aldrich Chemie GmbH, Eschenstraße 5, 82024 Taufkirchen, Germany.

15:15 - 15:30 **O-39. Matrix Modifiers to Improve SPME Performances for Analytes Heavily Bound to Biological Samples**

M. Tascon[1], G.A. Gómez-Ríos[2].

(1) Instituto de Investigación e Ingeniería Ambiental (IIIA-CONICET), Universidad Nacional de San Martín (UNSAM), San Martín, 1650 Buenos Aires, Argentina.
(2) 2Restek Corporation, 110 Benner Circle, Bellefonte, PA 16823, USA.

15:30 - 15:45 **Coffee Break**

Oral Session O8 **Chairs: S. Pedersen-Bjergaard, M. Miró**

15:45 - 16:00 **O-40. Hollow-Fiber Supported Liquid Membranes and Molecularly Imprinted Polymers as Solid Acceptor Phase for Highly Selective Extractions**

A. Martín-Esteban, E. Turiel, M. Díaz-Álvarez.

Departamento de Medio Ambiente y Agronomía. INIA. Carretera de A Coruña km. 7. 28040 Madrid. Spain.

16:00 - 16:15 **O-41. Biofluid Sampler: Beginning of a New Era of Mail-in-Analysis of Whole Blood Sample**

A. Kabir[1], A. Tartaglia[2], C. D'Ovidio[3], E. Rosato[2], H.I. Ulusoy[4], K.G. Furton[1], M. Locatelli[2].

(1) Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th St, Miami, FL 33199, USA.
(2) Department of Pharmacy, University of Chieti–Pescara "G. d'Annunzio", Via dei Vestini 31, Chieti 66100, Italy.
(3) Department of Medicine and Aging Sciences, Section of Legal Medicine, University of Chieti–Pescara "G. d'Annunzio", Chieti 66100, Italy.
(4) Department of Analytical Chemistry, Faculty of Pharmacy, Cumhuriyet University, Sivas 58140, Turkey.

16:15 - 16:30

O-42. Advances in Ionic Liquid-Based Sorbent Materials for Sample Preparation

J.L. Anderson.

Iowa State University, 1605 Gilman Hall, Ames, IA. 50011 USA.

16:30 - 16:50

PL2. EuChemS Division of Green and Sustainable Chemistry/ Compressed CO_2: An Attractive Green Solvent for the Preparation of Nanostructured Materials

N. Ventosa

Nanomol – TECNIO, Institut de Ciència de Materials de Barcelona (CSIC)-CIBER-BBN, Campus de UAB, 08193, Bellaterra, Barcelona, Spain

16:50 - 17:10

PL3. The Periodic Table of the Elements of Green and Sustainable Chemistry

P.T. Anastas[1,2]

(1) Yale University, School of the Environment, 195 Prospect St., New Haven, CT 06511, United States.

(2) Yale Center for Green Chemistry and Green Engineering, 370 Prospect St., New Haven, CT 06511, United States.

17:10 - 17:30

Closing ceremony and awards

Chairs: S. Ražić, E. Psillakis

Poster Sessions

Two parallel poster sessions (**PS-A** and **PS-B**) are scheduled on Thursday, 11 March (CET 13:00 - 14:00) and another two poster sessions (**PS-C** and **PS-D**) on Friday, 12 March (CET 13:00 - 14:00).

Thursday, 11 March 2021

13:00 - 14:00

PS-A Chairs: S. Ražić, M. Zoccali

P1. Capsule Phase Microextraction of Selected Polycyclic Aromatic Hydrocarbons from Water Samples Prior to their Determination by GC-MS

N. Manousi[1], A. Kabir[2], K.G. Furton[2], E. Rosenberg[3], G.A. Zachariadis[1].

(1) Laboratory of Analytical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece, nmanousi@chem.auth.gr.
(2) International Forensic Research Institute, Department of Chemistry and Biochemistry, Florida International University, Miami, FL, USA.
(3) Institute of Chemical Technology and Analytics, Vienna University of Technology, 1060 Vienna, Austria.

P2. Dispersive Liquid-Liquid Microextraction Based on the Solidification of the Floating Organic Droplet using a Menthol-Based Deep Natural Eutectic Solvent for the Extraction of Phthalic Acid Esters from Soft Drinks and Infusions

C. Ortega-Zamora[1], G. Jiménez-Skrzypek[1], J. González-Sálamo[1,2], J. Hernández-Borges[1,2].

(1) Universidad de La Laguna, Departamento de Química, Unidad Departamental de Química Analítica, Facultad de Ciencias, Avda. Astrofísico Fco. Sánchez, s/n°. 38206 San Cristóbal de La Laguna, Spain.
(2) Universidad de La Laguna, Instituto Universitario de Enfermedades Tropicales y Salud Pública de Canarias, Avda. Astrofísico Fco. Sánchez, s/n°. 38206 San Cristóbal de La Laguna, Spain.

P3. Determination of Drugs of Abuse in Saliva Samples via Dual-Template Molecularly Imprinted Paper and Direct Infusion Mass Spectrometry

M.C. Díaz-Liñán, M.T. García-Valverde, R. Lucena, S. Cárdenas, A.I. López-Lorente.

Departamento de Química Analítica, Instituto Universitario de Investigación en Química Fina y Nanoquímica IUNAN, Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie, E-14071 Córdoba, Spain.

P4. Magnetic Paper Sorptive Phase for the Extraction of Parabens and Triclosan from Swimming Pool Waters

F.A. Casado-Carmona, R. Lucena, S. Cárdenas.

Departamento de Química Analítica, Instituto Universitario Nanoquímica (IUNAN), Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie, E-14071, Córdoba, Spain.

P5. High Throughput Determination of Three Drugs of Abuse by Direct Infusion Mass Spectrometry Using Nylon-6 Coated Wooden Toothpicks

J. Millán-Santiago, R. Lucena, S. Cárdenas.

Departamento de Química Analítica, Instituto Universitario de Investigación en Química Fina y Nanoquímica (IUNAN), Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie, E-14071 Córdoba, Spain.

P6. Combining Nanotechnology and Ultrasound: In Situ Synthesis of Magnetic Nanocomposite for Mercury Preconcentration

I. De la Calle, J. Páez-Cabaleiro, V. Romero, I. Lavilla, C. Bendicho.

Centro de Invstigación Mariña, Universidade de Vigo, Departamento de Química Analítica e alimentaria, Grupo QA2, Edificio CC Experimentais, Campus de Vigo, As Lagoas, Marcosende 36310, Vigo, Spain.

P7. Development of Magnetic Nano-MIPs for the Selective Extraction of Proteins

B. Fresco-Cala, T. Rappold, B. Keitel, A.D. Batista, B. Mizaikoff.

Institute of Analytical and Bioanalytical Chemistry, Ulm University, 89081, Ulm, Germany.

P8. Preparation, Characterization and Application of C18 Thermally Immobilized onto Zirconized Silica as Sorbent for Solid-Phase Extraction

C.G.A. da Silva, T.S. Justiniano.

University of Mato Grosso (UFMT), Av. Fernando Correa da Costa, 2367, Boa Esperança, Cuiabá-MT, 78060-900, Brazil.

P9. Thermal and Ultrasound Pretreatments for Enhancing Phenolic Recovery from Different Grape Extracts

N. Dabetic, V. Todorovic, S. Sobajic.

Department of Bromatology, Faculty of Pharmacy, University of Belgrade, Vojvode Stepe 450, 11221 Belgrade, Serbia.

P10. µ-Separation of Petroleum Fractions Using a Metal-Organic Framework

J. Sundberg, K. Huynh, A.E. Jensen.

Centre for Oil & Gas, Technical University of Denmark, Elektrovej 375, 2800 Kgs. Lyngby, Denmark.

P11. Long-Term Evaluation of AAS Quality Control Data for Sample Preparation for Metal Analysis–Examples from Practice

J. Beljin, N. Duduković, K.Z. Tenodi, S. Maletić, S. Rončević.

Department of Chemistry, Biochemistry and Environmental Protection, Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovica 3, Novi Sad, 21000, Serbia.

P12. Hollow Fiber Membrane-Protected Molecularly Imprinted Microspheres for Micro Solid-Phase Extraction and Clean-Up of Thiabendazole in Citrus Samples

M. Díaz-Álvarez, A. Martín-Esteban, E. Turiel.

Departamento de Medio Ambiente y Agronomía. INIA. Carretera de A Coruña km. 7. 28040 Madrid. Spain.

P13. An Integrated Sample Preparation/Sensing Approach for Iodide Determination Involving Polyvinylpyrrolidone-Protected Copper Nanoclusters

F. Pena-Pereira, N. Capón, L. Placer, I. Lavilla, C. Bendicho.

Centro de Investigación Mariña, Universidade de Vigo, Departamento de Química Analítica e Alimentaria, Grupo QA2, 36310 Vigo, Spain.

P14. Surface Modified-Magnetic Nanoparticles by Molecular Imprinting For The Dispersive Solid-Phase Extraction of Triazines from Environmental Waters

E. Turiel, M. Díaz-Álvarez, A. Martín-Esteban.

Departamento de Medio Ambiente y Agronomía. INIA. Carretera de A Coruña km. 7. 28040 Madrid. Spain.

P15. Multi-Cumulative Trapping HS-SPME to Enhance the Volatile Profile of Extra-Virgin Olive Oil

S. Mascrez, **G. Purcaro.**

Gembloux Agro-Bio Tech, University of Liege, Passage des Déportés, 2, Gembloux, B-5030, Belgium.

P16. Vacuum-Assisted Headspace SPME: A Powerful Tool for Extra Virgin Olive Oil Profiling Enhancement

S. Mascrez[1], E. Psillakis[2], G. Purcaro[1].

(1) Gembloux Agro-Bio Tech, University of Liege, Passage des Déportés, 2, Gembloux, B-5030, Belgium.
(2) Laboratory of Aquatic Chemistry, School of Environmental Engineering, Technical University of Crete, Chania, Crete GR-73100, Greece.

P17. Improving the Performance of SPME Using Trap‐Based Preconcentration with Enrichmen

R. Szafnauer[1]**,** R. Cole[1], J.P. Mayser[1], N.D. Spadafora[1,2].

(1) Markes International Ltd, Gwaun Elai Medi-Science Campus, Llantrisant, RCT, CF72 8XL, UK.
(2) Department of Biology, Ecology and Earth Sciences, University of Calabria, Via Ponte P. Bucci 6b, 87036, Arcavacata Di Rende, Cosenza, Italy.

PS-B Chairs: R. Lucena, G. Purcaro

P18. Pressurized Hot Water Extraction Combined to SPME and GC×GC for Assessment of the Organic Fraction on Oil-bearing Source-rocks

B.J. Pollo[1], P.T.V. Rosa[1], F. Augusto[1,2].

(1) University of Campinas (UNICAMP), Cidade Universitária "Zeferino Vaz" 13083-970 Campinas-Brazil.
(2) National Institute for Science and Bionanalytical Technology (INCTBio), UNICAMP, Campinas-Brazil.

P19. FPSE-HPLC-PDA Method for Rapid Determination of Solar UV Filters in Human Whole Blood, Plasma and Urine

A. Tartaglia[1], M. Locatelli[1], C. D'Ovidio[2], E. Rosato[1], M. Bonelli[2], K.G. Furton[3], A. Kabir[3].

(1) Department of Pharmacy, University of Chieti–Pescara "G. d'Annunzio", Via dei Vestini 31, Chieti 66100, Italy.
(2) Department of Medicine and Aging Sciences, Section of Legal Medicine, University of Chieti–Pescara "G. d'Annunzio", Chieti 66100, Italy.
(3) Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th St, Miami, FL 33199, USA.

P20. Development of a Miniaturized Solid-Phase Microextraction Methodology for the Analysis of Volatile and Semivolatile Compounds in Honey

L. Vázquez[1], M. Celeiro[1], M. Sergazina[1,2], T. Dagnac[3], M. Llompart[1].

(1) CRETUS Institute. Department of Analytical Chemistry, Nutrition and Food Science, Universidade de Santiago de Compostela, E-15782, Santiago de Compostela, Spain.
(2) Department of Chemistry, Institute of Natural Science and Geography, Abai Kazakh National Pedagogical University, Almaty, Kazakhstan.
(3) Agronomic and Agrarian Research Centre (AGACAL-CIAM), Galician Agency for Food Quality, Unit of Organic Contaminants, Apartado 10, E-15080, A Coruña. Spain.

P21. Can Recycled Crumb Rubber Materials Spread Pollutants in Water? Evaluation of Water Leaches from Synthetic Turf Football Fields by HS-SPME-GC-MS/M

D. Armada[1], M. Celeiro[1], N. Ratola[2], T. Dagnac[3], J. de Boer[4], M. Llompart[1].

(1) CRETUS Institute, Department of Analytical Chemistry, Nutrition and Food Science, Universidade de Santiago de Compostela, E-15782, Santiago de Compostela, Spain.
(2) LEPABE Laboratory for Process Engineering, Environment, Biotechnology and Energy, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias S/n, 4200-465, Porto, Portugal.
(3) Agronomic and Agrarian Research Centre (AGACAL-CIAM), Galician Agency for Food Quality, Unit of Organic Contaminants, Apartado 10, E-15080, A Coruña. Spain.
(4) Vrije Universiteit Amsterdam, Department of Environment & Health, De Boelelaan 1085, 1081HV, Amsterdam, the Netherlands.

P22. Tropical Fruit Waste Valorisation Through Green and Sustainable Chemistry: Microwave Assisted Extraction

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P23. Optimization of Pressurized Liquid Extraction and Evaluation of Antioxidant, Anti-Inflammatory and Anti-Alzheimer Activities In Vitro of Ammodaucus Leucotrichus

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P24. Fabric Phase Sorptive Extraction of Tocopherols from Nut Oils Prior to Their High Performance Liquid Chromatographic Determination

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P25. Workflow for Integrated Quality and Safety Control of Dietary Supplements: Presence of Contaminants

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P26. Green Analytical Chemistry Principles in Anionic Surfactant Detection by Potentiometric Sensors

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P27. *No Sampling, the Best Sampling.* Noninvasive and Micro-invasive Strategies for Cultural Heritage Studies

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P28. Preconcentration of Selected Pesticides from Water Samples Using Coconut Shell Activated Carbon as Solid-Phase Extraction Adsorbent

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P29. Evaluation of Method Performances for Polycyclic Aromatic Hydrocarbons Analysis in Sediment Using Gas Chromatography/Mass Spectrometry

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P30. Utilization of DoE Approach to Optimize the Procedure of Modified Nucleosides and Deoxynucleosides Extraction for Targeted Metabolomic Analysis

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P31. Food Security in Wine Consumption

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P32. On-Line in-Syringe Ultrasound-Assisted Cloud Point-Dispersive Liquid–Liquid Microextraction for the Fluorescent Determination of Aluminum in Water and Milk Samples

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Friday, 12 March 2021
13:00 - 14:00

PS-C Chairs: M. Segundo, E. Psillakis

P33. A Molecularly Imprinted Polymer Based Electrochemical Sensor for the Determination of a Tyrosine Kinase Inhibitor Drug

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P34. The Influence of Disintegration Method on Metabolomics Analysis

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P35. Electrochemical Immunosensor for Determination of Glial Fibrillary Acidic Protein Using Screen-Printed Electrodes Modified with Au NPs/L-Cysteine

G. Ozcelikay[1], F. Mollarasouli[2], M.A. Unal[3], N. Karadas-Bakirhan[4], K. Gucuyener[5], E. Ergenekon[6], S.A. Ozkan[1].

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P36. FPSE Method for Sensitive Analysis of Venlafaxine Molecules in Urine Samples

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P37. Multiresidue Analysis of Antibiotics in Cereals by Liquid Chromatography Triple Mass Spectrometry

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P38. Determination of Seven Representative Antibiotics in Lettuce to Monitor Their Uptake

B. Albero, R.A. Pérez, J.L. Tadeo, M.M. Delgado, E. Miguel.

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P39. Fabrication of an Electrochemical Sensor for Determination of a Serotonin 5-HT3 Receptor Antagonist

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P40. Development of a Liquid-liquid Extraction Method for the Determination of Short Chain Fatty Acids from Bacteria Culture

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P41. A Nanocomposite Magnetic Core-Shell Material for Sensitive Analysis of Quercetin in Tea Samples by HPLC

S. Ulusoy[1], H.I. Ulusoy[2], Z. Erbas[3], E. Yilmaz[4], M. Soylak[3].

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P42. Native Fluorescent Natural Deep Eutectic Solvents for Green Sensing Applications: Curcuminoids in *Curcuma longa* Powder

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P43. Voltammetric Determination of Anticancer Drug Axitinib Using Boron-Doped Diamond Electrode

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P44. Andrew+ Automated Oasis 2x4 Mixed Mode Sorbent Selection SPE Protocol

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Waters Corporation, 34 Maple St, Milford, MA01757.

P45. Enhancing Laboratory Throughput Using Fully Automated High-Capacity Sorptive Extraction

R. Szafnauer, R. Cole, J.P. Mayser.

Markes International Ltd, Gwaun Elai Medi-Science Campus, Llantrisant, RCT, CF72 8XL, UK.

P46. A Straightforward and Semiautomated Membrane-based Method for the Determination of Cocaine and its Metabolites in Urine Samples Using LC-ESI-QTOF-MS

J. Merib[1], G. Mafra[2], L. Birk[1], C. Scheid[1], S. Eller[1], R. Brognoli[2], T. Franco de Oliveira[1], E. Carasek[2].

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P47. Trace Sibutramine Determination in Herbal Slimming Products

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P48. Detection of Cationic Surfactants in Disinfectants and Antiseptics by New Direct Potentiometric Surfactant Sensor

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PS-D Chairs: S. Ražić, M. Zoccali

P49. Comparison of Headspace Solid-Phase Microextraction High Capacity Fiber Coatings for Untargeted Analysis of Beer Volatiles Using GC-MS/VUV

D. Zanella[1], H.E. Anderson[2], T. Selby[2], R.H. Magnuson II[2], T. Liden[2], J.-F. Focant1, K.A. Schug[2,3].
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P50. LC-GC×GC-ToFMS/FID: A Powerful Technique for MOSH and MOAH Quantification and Characterization

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P51. Pristine and Functionalized Multi-Walled Carbon Nanotubes as Adsorbent Material for Solid-Phase Extraction of Multi-Class Organic Micropollutants

M.O. Barbosa, R.S. Ribeiro, A.R.L. Ribeiro, M.F.R. Pereira, A.M.T. Silva.
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P52. Sub-Ambient Temperature Sampling of Volatiles from Cheese Using Vacuum-Assisted Headspace Thin Film Microextraction and Solid Phase Microextraction

A. Pateraki, D. Tzanetou, E. Psillakis.

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P53. Leaching of PAHs and Nicotine from Heat-not-Burn Tobacco Products and Cigarette Butts

N. Solomou, M. Sotiropoulou, E. Fernández, E. Psillakis.

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P54. Use of Cork By-Products to Determine Fungicides in Water by SPE-GC-MS/MS Methodology

L. Vázquez[1], M. Celeiro[1], M. Sergazina[1,2], S. Docampo[1], T. Dagnac[3], V.J.P. Vilar[4], M. Llompart[1].
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P55. Fabric Phase Sorptive Extraction of Seven Parabens from Human Breast Tissues Prior to High-Performance-Liquid Chromatography – Photodiode Array Analysis of Cancerous and Non-Cancerous Samples

V. Alampanos[1], A. Kabir[2], K. Furton[2], Ž. Roje[3], I. V. Vrček[4], V. Samanidou[1].
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P56. Betaine-Based Natural Deep Eutectic Solvents as Promising Green Extraction Agents for Pesticides Determination in Valorized Food By-Products

B. Socas-Rodríguez, D.M. Alonso-García, J.A. Mendiola, A. Cifuentes, **E. Ibáñez.**
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P57. FPSE-HPLC-PDA Method for the Determination of Inflammatory Bowel Disease Treatment Drugs in Whole Blood, Plasma, and Urine

A. Kabir[1], K.G. Furton[1], C. D'Ovidio[2], E. Rosato[3], M. Bonelli[2], A. Tartaglia[3], M. Locatelli[3].
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P58. FPSE-HPLC-PDA Analysis of Seven Paraben Residues in Human Whole Blood, Plasma, and Urine

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P59. Assessment of Contaminants in Cereals with Different Degrees of Processing

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P60. Green Approach to Extraction of Plant Volatiles from Herbal Teas Using Ionic Liquids

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P61. Spinning Cup-Shaped 3D Printed Device for Immunoaffinity Microextraction of Diclofenac in Wastewaters

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P62. Solvent-Reducing Methods to Quantify Siloxanes in Wastewater and Sludge

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P63. Boronate Affinity Sorbents Based on Thiol-Functionalized Polysiloxane-Polymethacrylate Composite Materials in Syringe Format for Selective Extraction of Glycopeptides

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P64. Microwave-Assisted Saponification and SPE for the Simultaneous or Alternative Analysis of Dialkyl Ketones and Sterols in Fat

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P65. Vacuum-Assisted Headspace SPME Under Sub-Ambient Temperature for the Analysis of Fish Samples

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06. Abstracts of oral presentations

To Prepare or not to Prepare Samples: What is Necessary for a Green and Sustainable Extraction of Bioactive Compounds from Agro-Industrial Wastes

PL-1

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Keywords: *Extraction, Green and Sustainable Analytical Chemistry, Sample Preparation.*

Using green processes to extract bioactive compounds from agro-industrial waste based on a bio-circular economy model aiming towards the UN sustainable development goals is quite a new concept. Apart from a technical point of view that is intrinsically challenging to implement it, there is also a need to incorporate social criteria – e.g., to assign manufacturers' responsibilities for the life-cycles of products throughout the supply chain – related to institutional capacity building. This means understanding to what extent the institutional capacity created by agro-industrial symbiotic initiatives determines the transition from a linear to a bio-circular economy [1]. A circular economy model requires continuous material flow throughout the supply chain, avoiding the generation of waste by creating value to once neglected chemical substances and materials. This means creating strategies to ensure no loose ends in the material track, by recirculating waste streams within the supply chain or exploring new processes to transform or isolate new valuable products – processes that should be intrinsically benign (by design) [2]. The need to reduce waste generated by agroindustry, coupled with the great potential of this biomass to provide high added value compounds, justifies the importance of studying more sustainable ways to extract them from their complex matrices. Since the initial focus is to reduce environmental impact, it is important that the methodologies for such processes do not generate even more residue, which would be a paradox. However, to extract bioactive natural products from vegetal samples using green methodologies has been a challenge over the last decades, especially the scalable ones.

Developing new green technologies and exploring existing techniques to discover new scientific frontiers regarding sample preparation and the recovery of valuable compounds are important strategies towards sustainable development and valorisation of waste streams. Some important criteria that could be introduced into this context is known as sufficiency, a measure of something which is enough for a particular purpose, well connected to analytical chemistry. It is an approach that raises questions about what, together with, how much, in which ways that are necessary to produce something, avoiding what is superfluous or waste [3]. The idea behind these questions is to reduce consumption of raw materials and energy as far as possible by reducing the demand for goods and services, especially those requiring high levels of resource use. Therefore, in this presentation we will concentrate on the application of green and sustainable analytical chemistry principles – and related tools – to help find optimum parameters for sample preparation and extraction of bioactive compounds from some agro-industrial wastes using green extraction techniques as examples to illustrate our concepts [4].

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References

[1] V.G. Zuin, Circularity in green chemical products, processes and services: Innovative routes based on integrated eco-design and solution systems, Curr. Opin. Green Sustain. Chem. 2 (2016) 40-44.
[2] R.A. Milescu, M.L. Segatto, A. Stahl, C-R.McElroy, T. J. Farmer, J.H. Clark, V.G. Zuin, Sustainable Single-Stage Solid–Liquid Extraction of Hesperidin and Rutin from Agro-Products Using Cyrene, ACS Sustain. Chem. Eng. 8 (2020) 18245-18257.
[3] K. Kümmerer, J.H. Clark, V.G. Zuin, Rethinking chemistry for a circular economy, Science 367 (2020) 369-370.
[4] V.G. Zuin, L. Z. Ramin, M. L. Segatto, A. M. Stahl, K. Zanotti, M. R. Forim, M. F. G. F. Silva, J. B. Fernandes, To separate or not to separate: what is necessary and enough for a green and sustainable extraction of bioactive compounds from Brazilian citrus waste, *Pure Appl. Chem*. 93 (2021) 13-27.

Electromembrane Extraction – Sample Preparation Based on Electrokinetic Extraction Across a Supported Liquid Membrane

O-1

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Keywords: *Electromembrane extraction, Microextraction, Sample preparation*

Electromembrane extraction (EME) was introduced as a new microextraction concept for acidic and basic substances in 2006 [1]. Target substances are extracted from aqueous sample, through a supported liquid membrane (SLM), and into an aqueous acceptor solution. Extraction is forced by an electrical potential sustained over the SLM. The SLM separates the sample and the acceptor, and is compatible with complex samples such as blood, urine, beverages, and environmental waters. The acceptor typically is a pure buffer solution in water, and the volume is from 5 to 50 µL. For extraction of basic substances (cations), the cathode is in the acceptor, and the anode is in the sample. Both the sample and the acceptor are neutral (pH 7) or acidic, and keep the substances positively charged during EME. For extraction of acidic substances, the polarity of the electrodes is reversed, and pH is kept neutral or alkaline.

EME provides efficient sample clean up, and extraction selectivity is controlled by the chemical composition of the SLM, the direction and magnitude of the electrical potential, and sample and acceptor pH. Target substances can be extracted from sample volumes of 0.1-10 mL, and therefore EME provides enrichment. Acceptors are aqueous solutions, which can be injected directly in LC-MS without and evaporation and reconstitution in mobile phase. EME has been performed in 96-well format and in microchip systems, and has potential for automation and high-throughput applications [2]. The consumption of organic solvent per sample is 2-10 µL, and EME is therefore a green approach to sample preparation. EME is currently under commercial development, based on equipment where the electrical field is coupled through sample and acceptor containers of conducting polymer [3]. EME is an active field of research, and currently about 50 papers are published per year.

This presentation will give an overview of recent progress in EME and discuss the perspectives.

References

[1] S. Pedersen-Bjergaard, K.E. Rasmussen, Electrokinetic migration across artificial liquid membranes – New concept for rapid sample preparation of biological fluids, J. Chromatogr. A 1109 (2006) 291-307.

[2] N. Drouin, P. Kuban, S. Rudaz, S. Pedersen-Bjergaard, J. Schappler, Electromembrane extraction: Overview of the last decade, Trends in Analytical Chemistry 113 (2019) 357-363.

[3] 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.

Ionic Liquids: An “Old” Class of Chemicals of High Interest in Modern Sample Preparation and Analysis

O-2

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Keywords: *Biomolecular analysis, Gas chromatography, Ionic liquids, Sample preparation,*

Ionic liquids (ILs) were discovered by Paul Walden in 1914 while studying the properties of ethylamine salt of nitric acid, (m.p. 13–14°C) [1], and since the beginning, they have been the object of in depth studies in several disciplines of chemistry. ILs are organic salts liquid below 100°C and consists of an organic cation (in general N or P based) and an organic or inorganic anion. They are in general characterized by high thermal stability, negligible vapor pressure, unique solvating properties due to polarity and ionic character of molten salts, and, at the same time, of non-flammability, variable viscosities, conductivity, and miscibility in different solvents. ILs have enjoyed a remarkable success also in analytical and bioanalytical chemistry. Their properties are related to the electrostatic interactions of the analytes with the cationic and/or anionic moiety, which make ILs usable for many analytical applications and excellent alternatives to traditional organic solvents in many sample preparation procedures. At the same time, their possibility to be engineered provide them with an uncommon selectivity toward specific groups of compounds. The combination of these properties enables them i) to give high preconcentration rate for several sample preparation and detection applications [2,4], and ii) to provide excellent separation efficiency and peak capacities [2,3,5].

This lecture is a quick overview of the role ILs can play in an analytical procedure illustrated by examples from the authors' daily experience in sample preparation, and in biomolecular and gas chromatographic analyses mostly in the field of natural products and foods.

[1] P. Walden, Molecular weights and electrical conductivity of several fused salts. Bull. Acad. Imper. Sci. St. Petersbourg*, 8 (*1914) 405–422.
[2] Tien D. Ho, Cheng Zhang, L. W. Hantao, and J. L. Anderson, Ionic liquids in analytical chemistry: fundamentals, advances, and perspectives, Anal. Chem. 86 (2014) 262−285.
[3] A. Berthod, M.J. Ruiz-Ángel, S. Carda-Broch, Recent advances on ionic liquid uses in separation techniques, J. Chromatogr. A 1559 (2018) 2–16.
[4] K.D. Clark, M.J. Trujillo-Rodríguez, J.L. Anderson, Advances in the analysis of biological samples using ionic liquids. Anal Bioanal Chem. 410 (2018) 4567–4573.
[5] C. Cagliero, C. Bicchi, Ionic liquids as gas chromatographic stationary phases: how can they change food and natural product analyses? Anal. Bioanal. Chem. 412 (2020) 17-25.

In Situ Growth of Imidazolium-Based Porous Organic Polymer via Controlled Polymerization in Confined Space for In Vivo Microextraction

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Keywords: *In-situ growth; Porous organic polymer; Polymerization in confined space; In vivo monitoring*

In situ growth of sorbents on substrates has emerged as a valuable protocol for fabricating new extraction and chromatographic devices [1,2]. However, controlling the thicknesses and uniformities of sorbents in situ grown on substrates remains highly challenging. Herein, a novel in situ growth method for porous organic polymers (POPs) is developed by effectively controlling the in situ polymerization rate through the relatively slow diffusion of the precursors into the confined space within the capillary. As a result, stable and homogeneous POP coatings with the thicknesses controllable from several to tens micrometers were successfully grown on quartz fibers. Moreover, as the protonatable imidazolium building blocks were incorporated into the porous framework, the obtained POP coatings showed high extraction selectivity, fast extraction kinetics and excellent enrichment performance towards negatively charged molecules including dye and pharmaceuticals. Similar coatings for ionizable analytes are still relatively scarce in the literature compared to the coatings for lipophilic analytes. The POP coated microprobes were further applied for in vivo microextraction of pharmaceuticals in semi-solid fish muscle owing to the mechanical robustness of the POP coatings. The bioconcentration kinetics of these emerging organic pollutants in living fish was successfully revealed. The protocol presented here is promising for facilely preparing other uniform coatings based on POPs and probably even metal-organic frameworks.

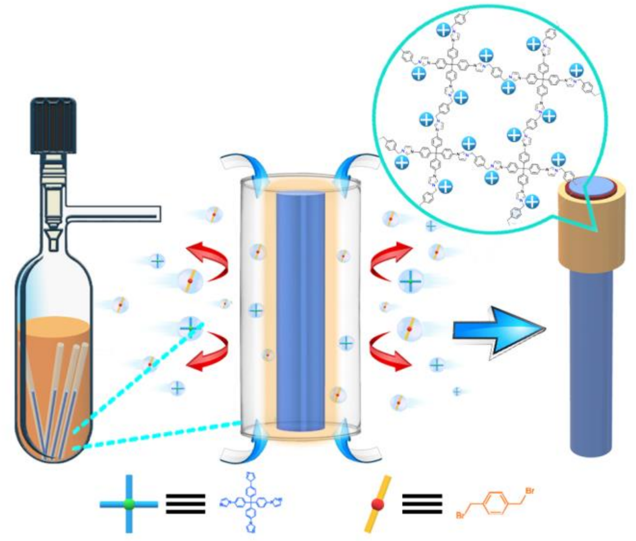

Figure 1. Schematic illustration of the controlled polymerization within the confined spaces in glass capillaries.

Acknowledgements

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References

[1] J. Guo, H. Qian, X. Zhao, C. Yang, X. Yan, In situ room-temperature fabrication of a covalent organic framework and its bonded fiber for solid-phase microextraction of polychlorinated biphenyls in aquatic products, J. Mater. Chem. A 7 (2019) 13249-13255.

[2] Q. Liu, N. Wang, J. Caro, A. Huang, Bio-inspired polydopamine: a versatile and powerful platform for covalent synthesis of molecular sieve membranes, J. Am. Chem. Soc. 135 (2013) 17679-17682.

Bead Injection as In-Line Renewable Solid-Phase Extraction Approach: Is There Room for Improvement?

O-4

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Keywords: *Automation, miniaturization, micro-solid-phase extraction, bead-injection, Lab-on-a-Valve.*

Bead injection analysis [1] is a mature sample preparation approach for flow-injection practitioners, yet it has not received a great deal of attention by the scientific community outside this niche. This lecture is aimed at outlining the fundamental principles and current state of the art progress of bead injection so as to attract the interest by the members of the EuChemS study group and network on sample preparation.

The first part of the lecture will gear toward analytical strategies for accommodation of sorptive microextraction approaches in a renewable/disposable bead-injection mode in which bead particles are processed alike fluids in flow conduits. This will be followed by illustrating the merits of allying bead injection with mesofluidic lab-on-valve (LOV) platforms that have proved suitable for in-line microsolid-phase extraction (μSPE) in a variety of areas of research endeavor in the bioanalytical field. A number of stringent requirements for the sorptive particles (beads) have been reported in the literature for repeatable handling in a bead-injection format and accepted as a paradigm, namely, the beads should be of perfect spherical shape (e.g., Sephadex or Sepharose-type or mixed mode hydrophobic-hydrophilic polymers), with uniform size distribution and density as close as possible to that of water. However, we will demonstrate that this is not valid anymore so as to expand the scope of the bead injection approach. Several examples will be selected so as to demonstrate the possibility of exploiting nanomaterials as renewable sorptive materials (also without magnetic properties) and the role of stereolithographic 3D printing [2] for fit-for-purpose LOV structures dedicated to bead injection protocols for clean-up of complex matrices (e.g., removal of phospholipids).

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References

[1] M. Miró, On-chip microsolid phase extraction in a disposable sorbent format using mesofluidic platforms, TrAC-Trends Anal. Chem., 62 (2014) 154-161.
[2] D.J.Cocovi-Solberg, M. Rosende, M. Michalec, M. Miró, 3D Printing: the second dawn of lab-on-valve fluidic platforms for automatic (bio)chemical assays, Anal. Chem. 91 (2019) 1140−1149.

Sustainable Supports for Microextraction

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Keywords: *Cotton, paper, wood*

Although considerable development arose in instrumental analysis in the last decades, sample preparation remains an inevitable step in many analytical methods. In fact, sample prep allows facing the challenges provided by the samples' complexity and the concentration thresholds established in many fields. Green Analytical Chemistry (GAC) principles identify these procedures as steps with a potential environmental impact due to the solvents, reagents, and energy consumed. Keeping in mind that our primary goal is to provide useful chemical information, sample preparation cannot be avoided entirely. However, we can make an effort to minimize the impact of our developments. In this sense, the minimization of the required resources, the automation and miniaturization of the procedures, and the use of renewable materials are more realistic objectives. In 2017, our research group (very recently renamed Affordable and Sustainable Sample Preparation) started a new line focused on applying lignocellulosic substrates in microextraction. The sustainability and worldwide availability of these substrates provide an added value, permitting their application in almost any laboratory. Whenever possible, the do-it-yourself (DIY) principle is applied, advocating for the importance of simplicity in sample preparation.

This communication will discuss the potential of cellulosic [1,2] (cotton and paper) and lignocellulosic (wood) [3] materials to design new sorptive phases in microextraction. These phases have been prepared following two different strategies. Dip-coating (and the somewhat related drop-casting technique) has allowed the modification of the substrates with commercial polymers, nanoparticles, and nanocomposites (Figure 1). However, the rich -OH surface of these substrates can be used to link some phases covalently, thus increasing the chemical stability of the coatings. Both approaches will be discussed in detail in the present communication.

The versatility of these phases will also be demonstrated with real applications. They can be applied in the classical extraction-chromatography-detection workflow, but other alternatives, like the direct combination to high-resolution mass spectrometry, are attractive to simplify the overall analytical procedure.

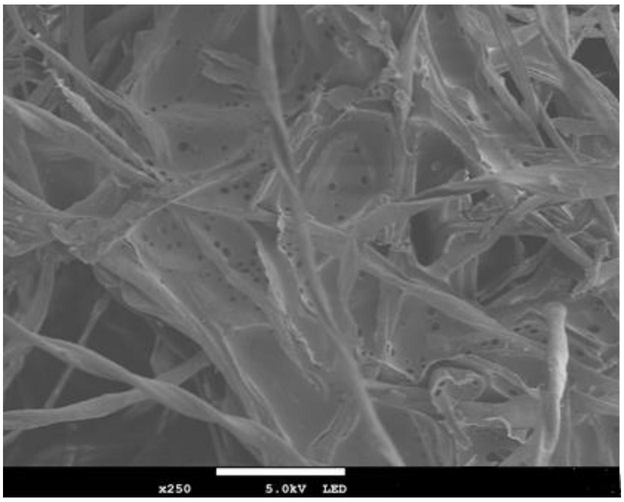

Figure 1. Scanning electron microscopy of cotton fibers modified with polystyrene

Acknowledgments

Financial support from the Spanish Ministry of Economy and Competitiveness CTQ2017-83175R is gratefully acknowledged

References

[1] M.T. García-Valverde, M.L. Soriano, R. Lucena, S. Cárdenas, Cotton fibers functionalized with β-cyclodextrins as selectivity enhancer for the direct infusion mass spectrometric determination of cocaine and methamphetamine in saliva samples, Anal. Chim. Acta 1126 (2020) 133-143.

[2] M.C. Díaz-Liñán, M.T. García-Valverde, R. Lucena, S. Cárdenas, A.I. López-Lorente, Dual-template molecularly imprinted paper for the determination of drugs of abuse in saliva samples by direct infusion mass spectrometry. Microchem. J. 160 (2021) 105686.

[3] J. Millán-Santiago, M. T. García-Valverde, R. Lucena, S. Cárdenas, Polyamide-coated wooden tips coupled to direct infusion mass spectrometry, a high throughput alternative for the determination of methadone, cocaine and methamphetamine in oral fluid, Microchem. J. 162 (2021) 105843.

Mixed-mode Amphoteric Materials to Solid-Phase Extract Ionisable Compounds from Environmental Waters

O-6

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Keywords: *mixed mode ion-exchange sorbents; amphoteric materials; solid-phase extraction; ionisable contaminants; environmental water samples*

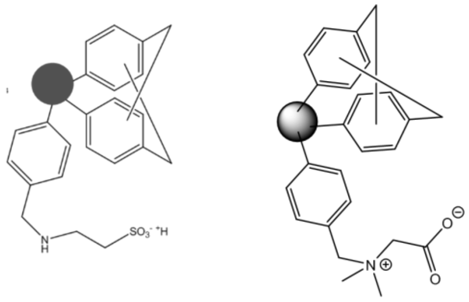
Mixed-mode ion-exchange materials combine silica- or polymer-based skeleton (reversed-phase interactions) functionalised with ionic moieties (ionic interactions with the ionic compounds). According to the moiety introduced, they are classified as strong cation-exchange (SCX), strong anion-exchange (SAX), weak cation-exchange (WCX) or weak anion-exchange (WAX). Since its emergence, they have been successfully applied in the selective extraction of different ionic compounds from complex samples [1,2]. Nevertheless, one of the main problems is the simultaneous extraction of analytes with acidic and basic properties. To solve this, one strategy is to functionalise the mixed-mode ion-exchange sorbents with amphoteric moieties that incorporate cation and anion-exchange moieties in the same functional group [3].

In this study, two hypercrosslinked amphoteric polymers have been developed for the retention of acidic and basic analytes simultaneously. They are functionalised with such moieties as sarcosine methyl ester further hydrolysed and methylated (quaternary amine and carboxylic acid) named HXLPP-SAX/WCX; and, with and taurine (secondary amine and sulfonic acid) named HXLPP-WAX/SCX. Figure 1 shows the structure of both sorbents.

The developed amphoteric sorbents were evaluated in the solid-phase extraction (SPE) followed by liquid chromatography with mass spectrometry in tandem (LC-MS/MS) for the selective determination of a group of acidic and basic compounds (including drugs and sweeteners) from environmental waters. The SPE parameters such as sample pH, washing and elution conditions were carefully optimised to exploit the ionic interactions between compounds and the functional groups. When loading 500 mL of ultrapure water followed by the optimised SPE protocol, both sorbents provided complete recoveries for all the compounds, with better results for HXLPP-SAX/WCX.

HXLPP-SAX/WCX was further validated and applied to the extraction of 250 mL of river and 100 mL effluent sewage waters with recoveries ranging from 52% and 93% for all the compounds, with the exception of mephedrone and methadone, and matrix effect lower than -30% in both samples thanks to the inclusion of a favourable washing.

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



HXLPP-WAX/SCX HXLPP-SAX/WCX

Figure 1. Structure of the developed mixed-mode amphoteric materials

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References

[1] N. Fontanals, F. Borrull, R.M. Marcé, Overview of mixed-mode ion-exchange materials in the extraction of orgànic compounds, Anal. Chim. Acta 1117 (2020) 89-107.
[2] L.M. Madikizela, S. Ncube, L. Chimuka, Recent Developments in selective Materials for solid phase extraction, Chromatographia 82 (2019) 1171–1189.
[3] J.C. Nadal, K.L. Anderson, S. Dargo, I. Joas, D. Salas, F. Borrull, P.A.G. Cormack, R.M. Marcé, N. Fontanals, Microporous polymer microspheres with amphoteric character for the solid-phase extraction of acidic and basic analytes, J. Chromatogr. A. 1626 (2020) 461348.

An Innovative Green Protocol for the Quantification of Benzothiazoles, Benzotriazoles and Benzenesulfonamide in PM10 Using Microwave-Assisted Extraction Coupled with Solid-Phase Microextraction Gas Chromatography Tandem-Mass Spectrometry

O-7

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Keywords: *emerging pollutants, green analytical chemistry, microwave-assisted extraction, particulate matter, solid-phase microextraction.*

Benzothiazoles (BTHs), benzotriazoles (BTRs), and benzenesulfonamide (BSAs) are high production volume chemicals used in several industrial and household applications. These compounds could be considered as new emerging pollutants because of their health concern and the lack of information about their presence in outdoor air samples. [1–4]. In this work, a new analytical method for the simultaneous quantification of BTHs, BTRs, and BSAs in PM10 was developed. The proposed protocol provides for the microwave-assisted extraction (MAE) of the analytes from the PM followed by solid-phase microextraction gas chromatography-tandem mass spectrometry determination (SPME-GC-MS/MS) [5]. Fourteen analytes representative for the three classes of compounds were considered.

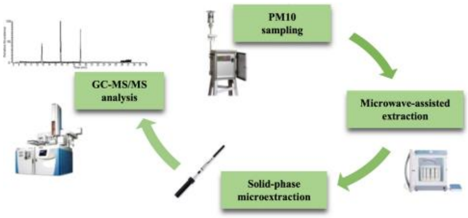

Figure 1. Graphical representation of the method workflow.

Usually, BTHs, BTRs, and BSAs have been extracted from particulate matter by using traditional approaches such as solid-liquid extraction [2,4] or more recently pressurized liquid extraction systems [1,3] using toxic organic solvents. In our method, we extracted the BTHs, BTRs, and BSAs by MAE using a green hydroalcoholic mixture composed by water and ethanol. Design of Experiment (DoE) was used for the multivariate optimization of the parameters affecting both the MAE extraction and the SPME analysis. A 2^{6-2} fractional factorial design was performed to determine the factors of the MAE, which have a significant influence on the analyte extraction. Later on, the most important variables were further optimized by central composite design (CCD), thereby achieving the optimal working conditions. The extraction performance of five SPME fibers was evaluated and the factors affecting the SPME extraction were optimized by CCD. The optimal working conditions were determined by using Derringer's desirability function. The analyte quantification was performed by using triple quadrupole mass spectrometry in selected reaction monitoring (SRM) acquisition mode. The proposed method was carefully validated following the guidelines issued by the international body. Satisfactory values were achieved in terms of linearity, accuracy, precision (intra- and inter-day), and lower limit of quantification.

References

[1] A. Maceira, F. Borrull, R.M. Marcé, Occurrence of plastic additives in outdoor air particulate matters from two industrial parks of Tarragona, Spain: Human inhalation intake risk assessment, J. Hazard. Mater. 373 (2019) 649–659.
[2] J. Asheim, K. Vike-Jonas, S. V. Gonzalez, S. Lierhagen, V. Venkatraman, I.L.S. Veivåg, B. Snilsberg, T.P. Flaten, A.G. Asimakopoulos, Benzotriazoles, benzothiazoles and trace elements in an urban road setting in Trondheim, Norway: Re-visiting the chemical markers of traffic pollution, Sci. Total Environ. 649 (2019) 703–711.
[3] A. Maceira, R.M. Marcé, F. Borrull, Occurrence of benzothiazole, benzotriazole and benzenesulfonamide derivates in outdoor air particulate matter samples and human exposure assessment, Chemosphere. 193 (2018) 557–566.
[4] M.L. Ferrey, M. Coreen Hamilton, W.J. Backe, K.E. Anderson, Pharmaceuticals and other anthropogenic chemicals in atmospheric particulates and precipitation, Sci. Total Environ. 612 (2018) 1488–1497.
[5] A. Naccarato, A. Tassone, S. Moretti, R. Elliani, F. Sprovieri, N. Pirrone, A. Tagarelli, A green approach for organophosphate ester determination in airborne particulate matter: Microwave-assisted extraction using hydroalcoholic mixture coupled with solid-phase microextraction gas chromatography-tandem mass spectrometry, Talanta. 189 (2018) 657–665.

Combining Headspace Microextraction Approaches with Miniaturized Detection Systems and IT Equipment for Determination of Anionic Species

O-8

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Keywords: *Anions, Microextraction, Non-instrumental detection; Optical sensing; Paper-based devices*

A remarkable trend in the analytical field is toward the development of rapid, straightforward and cost-efficient methods. In this sense, the use of miniaturized optical instruments and, more recently, everyday communications and information technology (IT) equipment offer novel opportunities for on-site detection [1], even though sensitivity and selectivity issues can arise. These limitations can be addressed by means of downsized sample preparation approaches, three-phase microextraction modes being particularly appealing for improved selectivity. More particularly, headspace microextraction offers substantial benefits, including an efficient clean-up, selective trapping of volatile analytes (or derivatives) and achievement of excellent enrichment factors. This work focuses on recent contributions involving *in situ* generation of volatiles, trapping and interaction/reaction of evolved derivatives with appropriate recognizing probes for determination of anionic species in an integrated manner. Thus, a number of analytical systems feasible for volatile sensing have been applied to the determination of relevant anions, namely iodide, bromide, nitrite, sulfide and arsenite [2-6]. Selected contributions involving the combination of headspace single-drop microextraction systems with portable, miniaturized optical detectors are initially discussed [2-4] and recent works devoted to the combination of headspace microextraction approaches involving cellulose substrates with non-instrumental devices are also considered [4-6].

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References

[1] K. Grudpan, S.D. Kolev, S. Lapanantnopakhun, I.D. McKelvie, Applications of everyday IT and communications devices in modern analytical chemistry: A review, Talanta 136 (2015) 84–94.

[2] F. Pena-Pereira, I. Lavilla, C. Bendicho, Unmodified gold nanoparticles for in-drop plasmonic-based sensing of iodide, Sens. Actuat. B 242 (2017) 940–948.

[3] F. Pena-Pereira, A. García-Figueroa, I. Lavilla, C. Bendicho, Ratiometric detection of total bromine in E-waste polymers by colloidal gold-based headspace single-drop microextraction and microvolume spectrophotometry, Sens. Actuat. B 261 (2018) 481–488.

[4] F. Pena-Pereira, N. Capón, I. de la Calle, I. Lavilla, C. Bendicho, Fluorescent poly(vinylpyrrolidone)-supported copper nanoclusters in miniaturized analytical systems for iodine sensing, Sens. Actuat. B 299 (2019) 126979.

[5] F. Pena-Pereira, L. Villar-Blanco, I. Lavilla, C. Bendicho, Test for arsenic speciation in waters based on a paper-based analytical device with scanometric detection, Anal. Chim. Acta 1011 (2018) 1–10.

[6] F. Pena-Pereira, Ó. Matesanz, I. Lavilla, C. Bendicho, A paper-based gas sensor for simultaneous noninstrumental colorimetric detection of nitrite and sulfide in waters, J. Sep. Sci. 43 (2020) 1908–1914.

Ionic Liquids for Micro-Scale Extractions from Plants: From the Plant Genome to the Plant Metabolome

O-9

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Keywords: *Ionic liquids, Plants, Metabolomics. Genomics*

Plants are a rich source of a wide variety of bioactive primary and specialized metabolites whose synthesis depends on the interaction between the plant genome and the environment. Analyses in the plant field have therefore to cover a wide range of topics from genomics to metabolomics, often dealing with very complex matrices. The development of an appropriate sample preparation method is therefore fundamental to obtain the required information, since the isolation and preconcentration of the target analytes are often challenging, also because downstream analyses will detect only the metabolites previously extracted. Although most studies on plants still adopt conventional extraction methods, new materials with improved features in terms of tunability, selectivity and, very important, sustainability have been developed in the past decades. In this context, ionic liquids (ILs) are very promising for the plant field. One of the main features of ILs is their ability to incorporate functional groups, within the IL structure, that selectively interact with specific analytes, ranging from nucleic acids to target classes of specialized metabolites. Moreover, ILs can incorporate a paramagnetic element into their structure giving rise to the magnetic ionic liquids (MILs), that can be easily separated with an external magnetic field, in a very rapid process thus avoiding centrifugation and filtration steps.

This presentation gives a rapid overview of the IL potential in the extraction of plant nucleic acids and specialized metabolites. In particular, the possibility to exploit MILs for very simple and fast extraction of genomic DNA from plants will be described **[1]** as well as the possibility to selectively extract specific sequences of plant DNA by ion-tagged oligonucleotides coupled with MILs **[2]**. At the same time, the adoption of IL-based surfactants will be discussed to show their potential for plant metabolomics investigations using the extraction of phenolic compounds from *Vitis vinifera* L. leaves as a case study **[3]**.

References

[1] A. Marengo, C. Cagliero, B. Sgorbini, J.L. Anderson, M.N. Emaus, C. Bicchi, C.M. Bertea, P. Rubiolo, Development of an innovative and sustainable one-step method for rapid plant DNA isolation for targeted PCR using magnetic ionic liquids, Plant Methods. 15 (2019) 1–11.

[2] A. Marengo, M. N. Emaus, C. M. Bertea, C. Bicchi, P. Rubiolo, C. Cagliero, J. L. Anderson, *Arabidopsis thaliana* ITS sequence-specific DNA extraction by ion-tagged oligonucleotides coupled with a magnetic ionic liquid, Anal. Bioanal. Chem. 411 (2019) 6583-6590.

[3] G. Mastellone, I. Pacheco-Fernández, P. Rubiolo, V. Pino, C. Cagliero, Sustainable Micro-Scale Extraction of Bioactive Phenolic Compounds from *Vitis vinifera* Leaves with Ionic Liquid-Based Surfactants, Molecules. 25 (2020) 3072.

Task Specific Ionic Liquids Based on 2-mercaptobenzothiazole for Selective Extraction of Cd

O-10

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Keywords: *Aqueous biphasic system, Cadmium, Extraction, Ionic liquids.*

Water is one of the most important resources on the planet, but industrial development and modern technologies have contributed to the pollution of natural water resources. Heavy metals are some of the most serious pollutants. Cadmium is a toxic heavy metal used in Ni-Cd batteries, the coloration of plastic and various discarded electronic products, and Cd released into the water system could causes serious health issues. Sample preparation is an important step in analysis of trace metals in complicated matrix such as environmental, biological and food samples. The room-temperature ionic liquids (ILs) are favorable alternative of organic solvents in liquid-liquid extractions, due to their distinctive tuned properties gained by careful selection of cation and anion, negligible vapor pressure and thus low flammability, broad liquids range, high solvation ability, high chemical and thermal stability, good extractability and selectivity for organic and inorganic compounds [1, 2]. In this study formation of aqueous biphasic systems (ABS) based on 1-alkyl-3-methylimidazolium ionic liquids with 2-mercaptobenzothiazole anions were studied as the new task specific ionic liquids (TSILs) suitable for one-step extraction of cadmium (II).

Two water soluble ILs: 1-butyl-3-methylimidazolium 2-mercaptobenzothiazole [bmim][mbt] and 1-ethyl-3-methylimidazolium 2-mercaptobenzothiazole [emim][mbt] were synthesized and applied in this study. The first, the novel ternary phase diagrams of the ABS composed of the IL, inorganic salts (potassium phosphate, citrate or chloride), and water at 293 K and pressure of 0.1 MPa were established. Then, the effect of ionic liquid cation, concentration of IL and inorganic salts on extraction efficiency was investigated.

[bmim][mbt] combining with K_3PO_4 has the highest ability to form ABS comparing to [emim][mbt] and citrate and chloride e.g. the lowest quantity of inorganic salt and IL are needed to build ABS (Fig. 1a). Since, one of the green chemical principles is using as lowest as possible quantity of chemicals, we selected [bmim][mbt] and K_3PO_4 for further experiments. Figure 1(b) shows the influence of amount of IL, [bmim][mbt], on extraction efficiency (E, %) and partition coefficient (K) on Cd(II) extraction. Increasing concentration of IL (4.5 – 17%) increase extraction efficiency (62-98%) and partition coefficient (12-37).

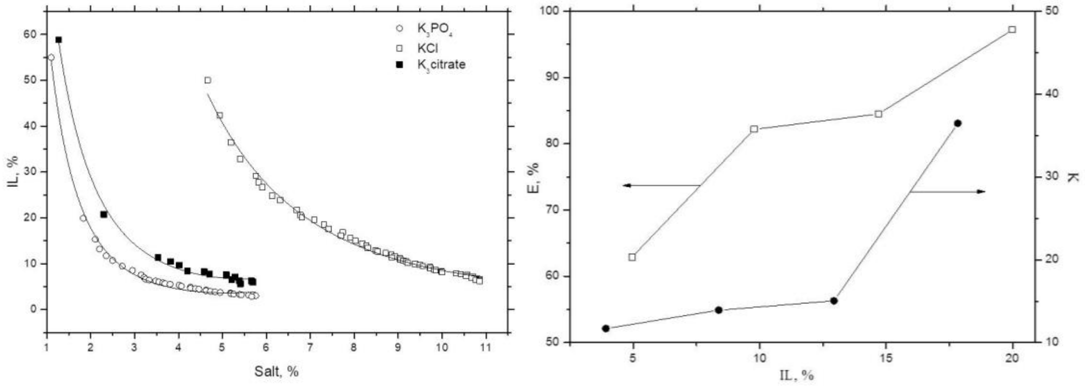

Figure 1. Effect of (a) inorganic salts on building ABS and (b) concentration of IL on extraction efficiency (E) and partition coefficient (K) of Cd(II)

This is the first results of extraction cadmium cation with task specific IL which is in the same time extractant and solvent. Additionally, ABS represents the green form of extraction without using organic solvents.

Acknowledgements
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References

[1] M.G. Freire (Ed.), Ionic-liquid-lased aqueous biphasic systems: fundamentals and applications, Springer-Verlag Berlin Heidelberg, Germany, 2016.

[2] T. Trtić-Petrović, A. Dimitrijević, N. Zdolšek, J.Đorđević, A. Tot, M. Vraneš, S. Gadžurić, New sample preparation method based on task-specific ionic liquids for extraction and determination of copper in urine and wastewater, Anal. Bioanal. Chem. 410 (2018) 155-166.

Modeling the Effect of Temperature on Solid-Phase Microextraction of Volatile Organic Compounds from Air Using Finite Element Analysis

O-11

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Keywords: *Air analysis, COMSOL, Modeling, SPME, VOCs.*

Headspace solid-phase microextraction (HS SPME) is considered as one of the simplest and cost-efficient sample preparation techniques for the determination of organic pollutants in environmental samples. Achieving the best combination of detection limits and accuracy requires careful optimization of about ten extraction and desorption parameters (fiber coating type, coating size, extraction temperature and time, pH, amount of salt added to the sample, sample/headspace ratio, agitation speed, pressure in the vial, desorption temperature and time, etc.), which can be time consuming, costly, and complex. Optimization of SPME is possible using COMSOL Multiphysics® (CMP) [1]. A possibility of optimization of sample and vial volumes [2], and pressure [3] in HS SPME was previously shown. This work was aimed at developing a model for optimization of temperature for SPME of volatile organic compounds (VOCs) from air. Benzene, toluene, ethylbenzene and m-xylene (BTEX) were chosen as a model group of analytes. The CMP model previously developed by us [3] was used with diffusion coefficients and coating-air distribution constants for analytes varying depending on extraction temperature. Diffusion coefficients at different temperatures were determined using the Fuller, Schettler and Giddings model. Distributions constants at different temperatures were determined using the Van't Hoff equation used by Arthur et al. [4]. The effect of a change in the enthalpy of vaporization of analytes with the increase of temperature to 90 °C was found to be insignificant. These models were chosen as the most accurate among models described in the literature. Modeling was conducted for 20-mL vials and 100 μm polydimethylsiloxane (PDMS) coating at temperatures 20-70 ºC. Extraction profiles of benzene from air at different temperatures were obtained (**Figure 1**). From the obtained results of the modelling, equilibration time decreases with the increase of extraction temperature. At 20 ºC, 99% of the equilibrium amount of benzene is extracted in 135 s, while at 70 ºC – in 118 s. Such difference would be difficult to detect during an experimental optimization. The developed model also allows modeling the effect of temperature at any chosen extraction time. Further research will be devoted to developing the model for HS SPME of VOCs from liquid and solid samples, where the developed model will be used to model diffusion of analytes in headspace and their partitioning between fiber and air.

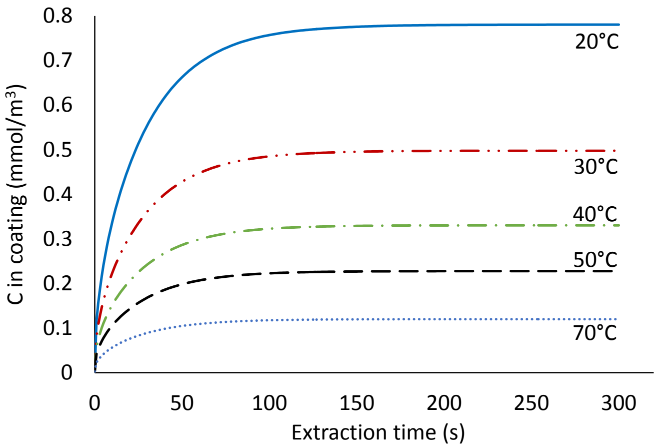

Figure 1. Effect of temperature (ºC) on benzene extraction profiles from air by 100 μm PDMS coating modeled using COMSOL.

Acknowledgements
This research was funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No. AP08052684).

References

[1] M.N. Alam, L. Ricardez-Sandoval, J. Pawliszyn, Numerical modeling of solid-phase microextraction: binding matrix effect on equilibrium time, Anal. Chem. 87 (2015) 9846-9854.
[2] B. Kenessov, M. Derbissalin, J.A. Koziel, D.S. Kosyakov, Modeling solid-phase microextraction of volatile organic compounds by porous coatings using finite element analysis, Anal. Chim. Acta 1076 (2019) 73-81.
[3] A. Zhakupbekova, N. Baimatova, B. Kenessov, A critical review of vacuum-assisted headspace solid-phase microextraction for environmental analysis, Trends Environ. Anal. 22 (2019) e00065.
[4] C.L. Arthur, L.M. Killam, K.D. Buchholz, J. Pawliszyn, J.R. Berg, Automation and optimization of solid-phase microextraction, Anal. Chem. 64 (1992) 1960-1966.

The Impact of Solid Phase Microextraction (SPME) Adsorbent Properties on Analytical Performance

O-12

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Keywords: *solid phase microextraction, SPME, sample preparation*

Solid-phase microextraction (SPME) is a fast, sensitive, and solvent-free technique for the extraction of analytes from gas, liquid, and solid samples. SPME uses a fiber coated with a liquid polymer, a solid sorbent, or a combination of both. The fiber coating extracts the compounds from the sample by absorption in the case of liquid coatings or adsorption in the case of solid coatings. In this work we examine different adsorbent materials in order to address the influence of particle structure and properties on extraction and desorption behavior. Briefly, average area responses from a mixture of 10 analytes encompassing a range of molecular weights and polarities were compared using commercially available carbon and divinyl benzene (DVB) based SPME devices. Carbon adsorbents containing micropores were found to provide improved retention of small polar and to a lesser degree, non-polar analytes (Figure 1) and an overall improvement in desorption efficiency was achieved even at reduced coating volumes. Micropores were similarly found to provide improved retention of the analytes of interest for DVB-coated adsorbent SPME fibers. This information can be utilized in order to ensure the correct SPME fiber coating is selected for the specific analyte(s) of interest.

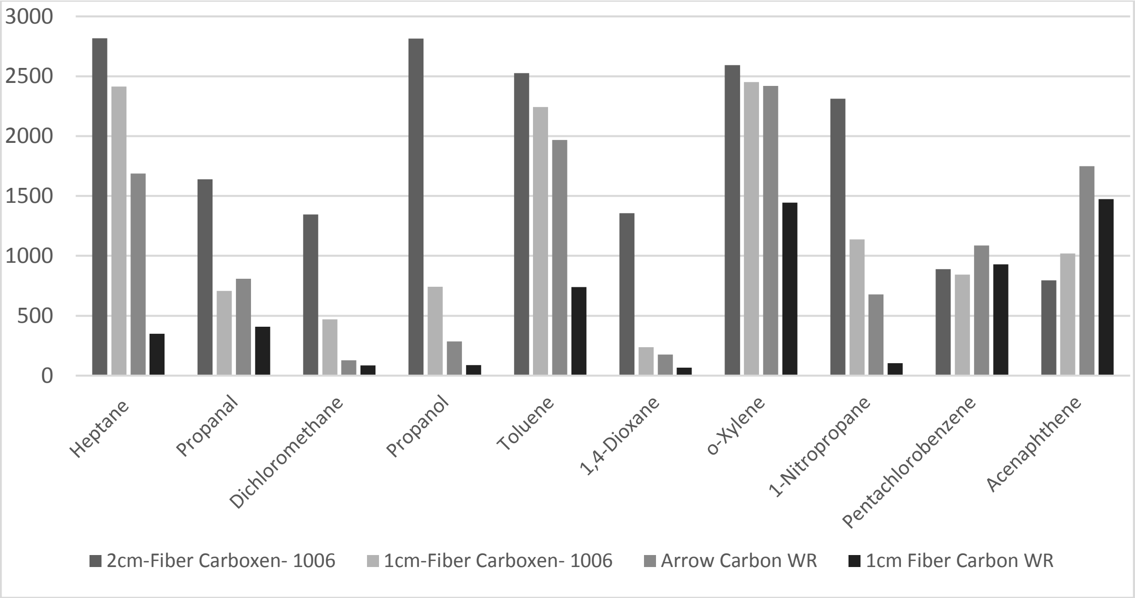

Figure 1. Comparison of average area response for 10 analytes ranging in molecular weight from 58-260 AMU and log Kow from -0.5 to 6.8 on a 2 cm Carboxen-1006 SPME fiber, 1 cm Carboxen-1006 SPME fiber, 1 cm carbon WR SPME fiber, and carbon WR SPME arrow devices.

Asking Better Questions in Microextraction

O-13

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Keywords: *vortex-assisted liquid-liquid microextraction; vacuum-assisted microextraction; fundamentals*

Sample preparation scientists use a variety of methods and instruments to try to answer two basic questions directly related to qualitative and quantitative analysis: “what have I got?” and “how much of it do I have?”. Questions like “why did I obtained this result?” or “how did this happen?” are rarely asked; yet these questions are the ones that bring the science in everything they do. Next to all the application-driven research carried out in separation science, sample preparation scientists need to have a strong science focus and always aim describing the fundamentals behind microextraction methods.

This contribution discusses how asking unconventional questions led our group obtaining several unexpected results and helped us better understand underlying phenomena. Initially, the case of vortex-assisted liquid-liquid microextraction (VALLME) is presented where vortex agitation to disperse microliters of the extracting solvent into the aqueous sample [1]. The seemingly easy steps of VALLME involve extremely complex and poorly understood processes that require consideration of solvent drop breakup and coalescence plus the problem of interphase analyte mass transfer. The fundamental hydrodynamic and interfacial science concepts of emulsion formation and phase separation in VALLME are used to improve current fundamental understanding of VALLME. The effects of several experimental parameters on VALLME are then discussed by integrating multiple perspectives from fluid dynamics, interfacial science and mass transfer in knowledge gained from past VALLME applications. The effect of surfactant addition during VALLME is also presented to the extent allowed by existing experimental VALLME data.

In the second part, the clear benefits of adopting the vacuum approach [2] are presented through the discussion of several new applications from different collaborations. Initially, a new Vac-HSSPME method for the analysis of perishable food samples is discussed. The results showed that Vac-HS-SPME sampling under vacuum at 5°C yielded similar extraction efficiencies to those obtained with standard HS-SPME at 40°C. This is the first time that such a high sensitivity can be achieved at such a low sampling temperature, opening the door to new applications for the quality control of perishable foods. Sampling under vacuum was found particularly beneficial not only for SPME but also for headspace microextraction methods using higher capacity extracting phases. An overview of the results and underlying mechanisms with vacuum-assisted headspace single-drop microextraction, vacuum-assisted headspace sorptive extraction (Twisters) and thin film microextraction (TFME) is given. The analysis demonstrates the pressure dependence of the underlying processes and predicts the superior performance of each method when sampling under vacuum.

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References

[1] E. Psillakis, Vortex-assisted liquid-liquid microextraction revisited, TrAC-Trends in Anal. Chem. 113 (2019) 332-339.
[2] E. Psillakis, The effect of vacuum: an emerging experimental parameter to consider during headspace microextraction sampling, Anal. Bioanal. Chem. 412 (2020) 5989-5997.

Microfluidic Paper-Based Analytical Devices for Sample Preparation and Rapid Detection

O-14

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Keywords: *Microfluidic paper-based analytical devices, Loop-mediated isothermal amplification, sample preparation, rapid detection*

Microfluidic paper-based analytical devices (μPADs) integrate the experimental processes of sample pretreatment, separation, analysis and detection on the same device, so as to achieve the goals of miniaturization, automation, low consumption and high efficiency. A layer of hydrophilic cellulose fibers was used in μPADs to move liquid samples from the inlet to the outlet where biological or chemical reactions occur. This directional flow facilitates the ability to perform complex sample preparation steps and suggests their promising applications in multiplex detection of pathogens and pollutants. Loop-mediated isothermal amplification (LAMP) is a promising method introduced recently for rapid detection, which relies on an auto-cycling strand displacement DNA synthesis performed by the Bst DNA polymerase. Therefore, we are inspired to develop devices which combine μPADs with LAMP for rapid detection of pathogens and bacteria. We first demonstrated the multiplex determination of microbial species from whole blood, using the μPAD technique to enable DNA extraction, LAMP and array-based fluorescence detection, for identification of three species of Plasmodium [1]. We then further developed this μPAD for the detection of three bovine infectious reproductive diseases in semen samples from rural India [2]. Detection limits of the device were as low as 50 Leptospira organisms, 50 CFU Brucella, and 1 TCID50 BoHV-1. Later, we developed the μPAD to enable multiplex assays for malaria and field trials in Uganda. Our device shows a sensitivity of 98% for malaria from infected individuals, which is more sensitive than optical microscopy (86%) and industry standard rapid immunodiagnostic tests (83%) [3]. Recently, we developed a μPAD for rapid detection of bacteria in drinking water and SARS-CoV-2 in wastewater [4]. After systematic optimization of μPAD, our device was able to detect Salmonella, E. Coli and C. Perfringens at ~ 100 copies DNA per reaction. Therefore, μPADs can be integrated into a field-ready module for sensitive and selective detection, which provide a powerful platform for sample preparation and rapid detection of diseases and microbial contamination, especially in the resource-limited regions.

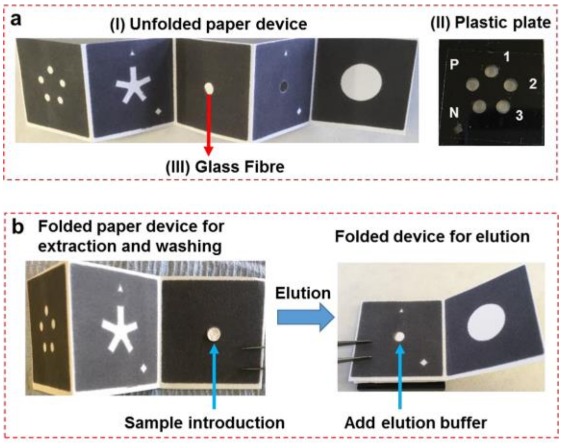

Figure 1. Design of the paper device for the detection of 3 targets.

References

[1] G. Xu, D. Nolder, J. Reboud, M.C. Oguike, D.A. van Schalkwyk, C.J. Sutherland, J.M. Cooper, Paper Origami Based Multiplexed Malaria Diagnostics from Whole Blood, Angew.Chem.Int. Ed. 55 (2016) 15250–15253.

[2] Z. Yang, G. Xu, J. Reboud, S.A. Ali, G. Kaur, J. McGiven, N. Boby, P.K. Gupta, P. Chaudhuri, J.M. Cooper, Rapid Veterinary Diagnosis of Bovine Reproductive Infectious Diseases from Semen Using Paper-Origami DNA Microfluidics. ACS Sens. 3 (2018) 403−409.

[3] J. Reboud, G. Xu, A. Garrett, M. Adriko, Z. Yang, E.M. Tukahebwa, C. Rowell, J.M. Cooper, Paper-based microfluidics for DNA diagnostics of malaria in low resource underserved rural communities. PNAS 116 (2019) 4834-4842.

[4] K. Mao, H. Zhang, Z. Yang, Can a Paper-Based Device Trace COVID-19 Sources with Wastewater-Based Epidemiology?, Environ. Sci. Technol. 54 (2020) 3733-3735.

Miniaturized Active Air Sampling Method for the Analysis of Tire Rubber Pollutants from Indoor and Outdoor Places

O-15

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Keywords: *Air analysis, gas chromatography-tandem mass spectrometry, polycyclic aromatic hydrocarbons, solid-phase extraction, tire rubber*

Tire rubber is a continuous source of pollution especially significant in high traffic density urban areas. Recycled tire crumb rubber is employed to manufacture sport and leisure facilities such as infill in synthetic turf football fields and playgrounds. The presence of high number of contaminant substances (polycyclic aromatic hydrocarbons, heavy metals, endocrine disruptors, plasticizers, antioxidants, vulcanisation additives, etc) in tire rubber and in crumb rubber surfaces have been demonstrated in outdoor and indoor environments [1, 2, 3].

The main goal of this work is the development of a miniaturized methodology based on solid-phase extraction (SPE) followed by ultrasound assisted extraction (US) and gas chromatography coupled to tandem-mass spectrometry (GC-MS/MS) analysis for the simultaneous sampling and analysis of 41 compounds including PAHs, plasticizers (phthalates, adipates and bisphenol A), antioxidants and vulcanisation tire rubber additives in air [4]. Sorbent amount (25 and 50 mg) and type of sorbent (Tenax TA, MIL-101 and Florisil) were evaluated as preliminaty studies. Most critical parameters (i.e. type of sorbent, type of solvent, time and desorption technique) were optimized by a multifactorial experimental design to obtain the highest extraction and sorbent desorption.

After selecting the best conditions for the sampling and extraction step, breakthrough volume was evaluated demonstrating that it does not occur in the studied interval (0.5 to 4 m^3). The optimal conditions involved the use of 25 mg of Tenax TA, 1 mL of solvent (ethyl acetate), 2 min of US.

The performance of the method was evaluated in terms of linearity, repeatability, accuracy and precision. Recoveries were studied at two levels (20 and 200 ng m^{-3}), obtaining quantitative results with values ranging between 71-110%, and relative standard deviation, RSD, values lower than 17%. Limits of detection at the low and sub ng m^{-3} were achieved. Finally, the validated SPE-GC-MS/MS method was applied to analyse different air samples from indoor and outdoor environments, including synthetic turf football pitches.

Acknowledgements

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References

[1] M. Celeiro, D. Armada, T. Dagnac, J. de Boer, M. Llompart, Hazardous compounds in recreational and urban recycled surfaces made from crumb rubber. Compliance with current regulation and future perspectives, Sci. Total Environ. 755 (2020) 142566.
[2] K. Schneider, M. de Hoogd, P. Haxaire, A. Philipps, A. Bierwisch, E. Kaiser, ERASSTRI-European Risk Assessment Study on Synthetic Turf Rubber Infill–Part 2: Migration and monitoring studies, Sci. Total Environ. 718 (2020) 137173.
[3] C. Dye, A. Bjerke, N. Schmidbauer, S. Manø, Measurement of air pollution in indoor artificial turf halls. Norwegian Inst Air Res Report NILU OR, 3, 2006.
[4] D. Armada, M. Celeiro, A. Martinez-Fernandez, P. Nurerk, T. Dagnac, M. Llompart, Miniaturized active air sampling method for the analysis of tire rubber pollutants from indoor and outdoor places, J. Sep. Sci. (2021). https://doi.org/10.1002/jssc.202001249.

Column witching for Automated Online Enrichment and Separation of Polar and Nonpolar Analytes from Aqueous Matrices

O-16

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Keywords: *2D-LC, column switching, online enrichment, separation, water contaminants*

Trace substances in surface water pose great challenges for instrumental analysis [1]. This is due to the low concentration and to the wide range of polarities of the analytes. To significantly increase the concentration of analytes for detection, they can be enriched on solid phase extraction materials. The different polarities are addressed by varying the selectivity of the solid phase extraction material. Usually, the enrichment of the analytes is done offline. Here, sample preparation must be repeated with different solid phases depending on the polarity spectrum of the analytes. This requires a considerable amount of time and effort. Sometimes, manual performance results in reduced recovery [2]. In this work, a concept for online enrichment and online separation was developed that significantly reduced the effort of the offline method.

For this purpose, ten model analytes covering a logP range from -4 to +6 were dissolved in water. This solution was directly loaded onto the reversed phase (RP) column (Figure 1 a, black flow path) using large volume injection (LVI). While the nonpolar analytes were focused at the column head, the polar analytes eluted to the porous graphitized carbon (PGC) column and were enriched there. To detect analytes that could not be enriched on either column, the waste output was monitored with a mass selective detector (MSD). After this enrichment step, the 2D-LC valve switched so that the nonpolar analytes could be separated on the RP column by gradient elution and detected in the MSD (Figure 1 b, black flow path). After the nonpolar separation is finished, the polar analytes were eluted from the PGC column by gradient elution and separated on the hydrophilic interaction liquid chromatography (HILIC) column and detected in the MSD (Figure 1 b, dark gray flow path).

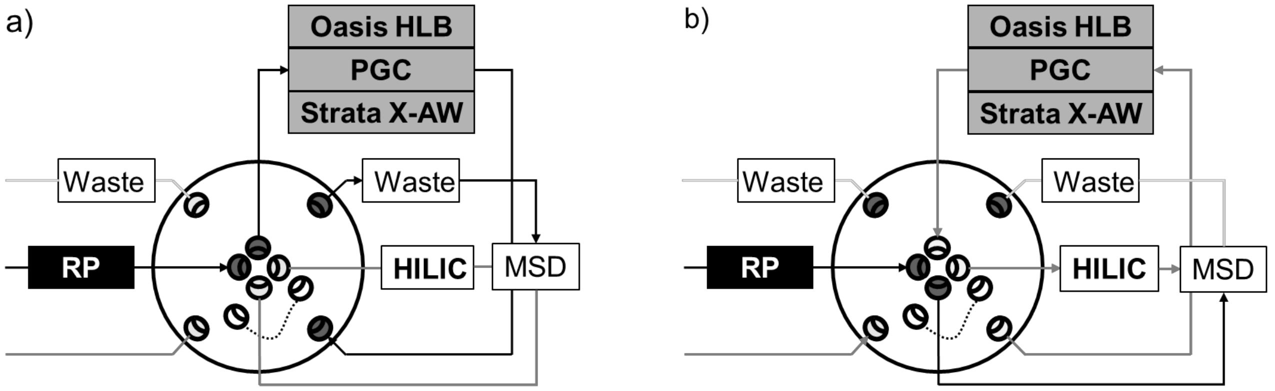

Figure 1. Column switching scheme. a) black flow path: Enrichment of the nonpolar analytes (RP column) and polar analytes (PGC column). b) Black flow path: separation of the non-polar analytes (RP column), Light gray flow path: separation of the polar analytes (HILIC column).

At a flow rate of 0.4 mL/min for 15 minutes, 6 mL of sample could be enriched without any loss of analytes. Subsequent separation was performed for all analytes with a retention factor > 10. If the polar analytes, due to the aqueous front from the PGC column, do not experience retention on the HILIC column, organic solvent can be added directly in front of the HILIC column by using the bypass (Figure 1 b, dotted line).

If the PGC or RP phases are not suitable for the preconcentration of all target analytes, further stationary phases can be screened automatically for the preconcentration of those analytes by means of column selection valves. The enrichment can be permanently monitored with the MSD.

Acknowledgements

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References

[1] EU, Communication from the comission to the european parliament, the council and the european economic and social comittee; European Union Strategic Approach to Pharmaceuticals in the Environment; Brussels, 11.3.2019, COM(2019) 128 final

[2] A. Andrade-Eiroa, M. Canle, V. Leroy-Cancellieri, V. Cerdà, Solid-phase extraction of organic compounds: A critical review. Part II, TrAC-Trends Anal. Chem. 80 (2016) 655–667.

Chromatographic Fingerprinting and Accurate Quantitative Profiling by Multiple Headspace Solid Phase Microextraction and Differential-Flow Modulated Comprehensive Two-Dimensional Gas Chromatography: The Aroma Blueprint of Extra Virgin Olive Oil

O-17

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Keywords: *Comprehensive two-dimensional gas chromatography, Parallel detection MS/FID, Predicted relative response factors, Quantitative analysis, Reverse-inject differential-flow modulation*

The role of sample preparation, as key-step of the analytical method and as zeroth dimension of the system, is crucial and its design is strictly dependent on the method's final objectives (*e.g*., untargeted fingerprinting or targeted profiling). In the study of the complex food volatilome, comprehensive two-dimensional gas chromatography combined to mass spectrometric detection (GC×GC-MS), has demonstrated to be very effective on both untargeted and targeted investigations, while combining high-throughput fingerprinting to quantitative profiling on the same analytical batch [1].

In this study we make a step forward in the exploitation of headspace solid-phase microextraction (HS-SPME) GC×GC-MS potentials, by designing a procedure capable of performing a comprehensive chromatographic fingerprinting of the complex volatile fraction of high-quality extra-virgin olive oil (EVOO) while providing accurate quantitative data on a large set of targeted analytes (*i.e*., targeted quantitative profiling [2]) with an informative role related to samples sensory quality and qualification – the so called *aroma blueprint* [3]. Moreover, the procedure is designed for full automation and is based on robust, reliable, commercially available analytical platform, suitable for high-throughput screenings and quality control assessment.

For these reasons, the differential-flow modulation technology is here chosen as core element of the GC×GC platform, because of its stable performances and relative ease of use [2]. On the other hand, to achieve accurate quantitative results accompanied by low limits of quantitation (LOQs), the multiple headspace extraction (MHE) approach is combined to the enrichment capacity of SPME with a multi-component fiber. The challenging aspect of the MHS-SPME procedure rely on the need of avoiding headspace saturation, at the basis of quantitation inaccuracy of some HS methods, while enabling multi analyte quantitation with a relatively simple calibration procedure.

Method's figures of merit include analytes identity confirmation, by EI-MS spectral signature and two retention time points (${}^{1}t_R$ and ${}^{2}t_R$), and accuracy in quantitative determinations based on external calibration and results cross-validation within two paralleled detectors (i.e., MS and flame ionization detector FID). Moreover, parallel detection by MS/FID, enables the extension of the method linearity range over three order of magnitude and opens to the possibility of adopting predicted FID relative response factors (RRFs) for quantitative estimations.

Results are critically evaluated in light of their fingerprinting potential over a set of fifty EVOO samples from Italian top-quality production [5], obtained from different olives cultivars and from three harvest regions. Quantitative data on 39 targeted analytes are compared to those achieved by applying single level internal standardization (IS), which does not consider, above all, analytes HS partition constants (K_{HS}) and accumulating polimer/material distribution constant (K_D) under the applied sampling conditions. The aroma blueprint of EVOOs from Garda lake region, Sicily and Tuscany is therefore delineated and the signature of quality objectified.

References

[1] F. Stilo, C. Bicchi, A.M. Jimenez-Carvelo, L. Cuadros-Rodriguez, S.E. Reichenbach, C. Cordero, Chromatographic fingerprinting by comprehensive two-dimensional chromatography: Fundamentals and tools, TrAC - Trends Anal. Chem. 134 (2021) 116133.
[2] F. Stilo, C. Bicchi, A. Robbat, S.E. Reichenbach, C. Cordero, Untargeted approaches in food-omics: the potential of comprehensive two-dimensional gas chromatography/mass spectrometry, TrAC Trends Anal. Chem. 135 (2020) 116162.
[3] A. Neugebauer, M. Granvogl, P. Schieberle, Characterization of the Key Odorants in High-Quality Extra Virgin Olive Oils and Certified Off-Flavor Oils to Elucidate Aroma Compounds Causing a Rancid Off-Flavor, J. Agric. Food Chem. 68 (2020) 5927–5937.
[4] J. V. Seeley, N.J. Micyus, S. V. Bandurski, S.K. Seeley, J.D. McCurry, Microfluidic deans switch for comprehensive two-dimensional gas chromatography, Anal. Chem. 79 (2007) 1840–1847.
[5] Fondazioni in Rete per la Ricerca agroalimentare AGER, project Violin “Valorization of Italian olive oil production by advanced analytical tools” 2016.

Working Towards Comprehensive Steroid Detection in Urine via Targeted MIPs Clean-up and Fully Automated GCxGC-MS Analysis.

O-18

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Keywords: *Anti-doping, GCxGC, Solid Phase Extraction (up to 5 keywords in Alphabetical order)*

Steroid doping remains a significant problem within the world of competitive sport. In the most recent figures published (2019, published December 2020) androgenic anabolic steroids (AASs) were responsible for 44 % of analytical adverse findings (AAFs, 1825 of 4180, Figure 1);[1] highlighting the need for continued research into this field. Throughout history there has been many high-profile cases (e.g. the THG BALCO scandal). One of the problems is the inability to detect new, unknown compounds (that are constantly appearing). To date, there are over 60 AASs on the WADA prohibited list.[2] In this talk I describe the design, synthesis and use of molecular imprinted polymers (MIPs) for compound specific solid phase extraction (SPE) to clean up an otherwise dirty, complex matrix as part of a screening test for banned steroids using GCxGC to overcome this problem.

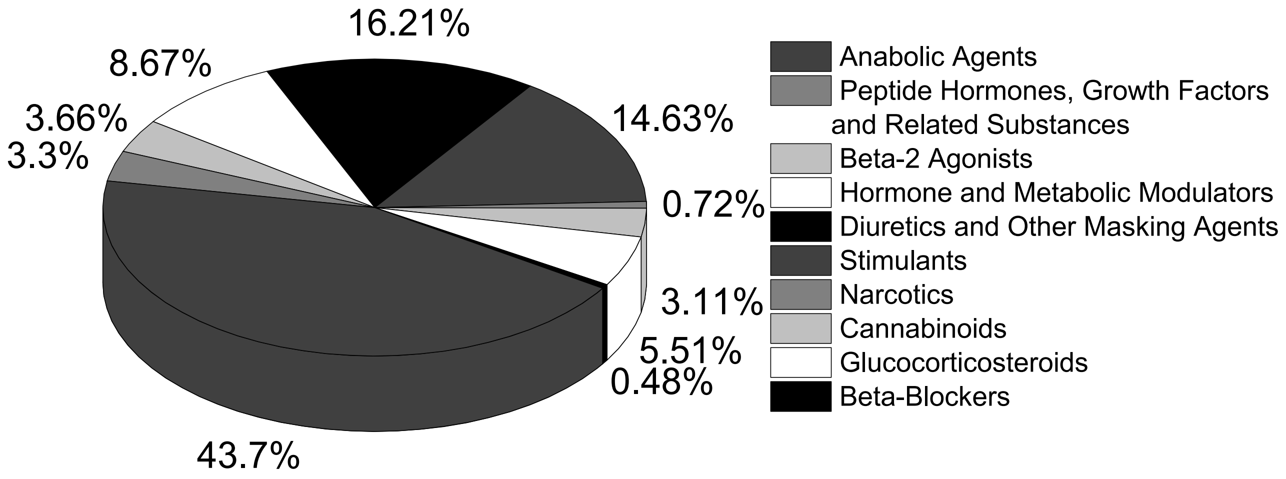

Figure 1. Substances Identified as AAFs in Each Drug Class in ADAMS (All Sports), data from the WADA 2019 Anti-doping Testing Figures. [1, 3]

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References
[1] World Anti-Doping Agency (WADA), 2019 Anti-Doping Testing Figures, (2020).
[2] World Anti-Doping Agency (WADA), Prohibited List, (2021).
[3] R.A. Hand, E. Piletska, T. Bassindale, G. Morgan and N. Turner, Application of Molecularly Imprinted Polymers in the Anti-Doping Field: Sample Purification and Compound Analysis, Analyst 145 (2020) 4716-4736.

Lab-In-Syringe Automated Double-Stage Extraction for the Determination of Sulfonamides Antibiotics in Urine

O-19

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Keywords: *homogeneous liquid-liquid extraction, Lab-In-Syringe, online solid-phase extraction, sulfonamides, urine*

Lab-In-Syringe (LIS) technique [1] is a flow-batch approach combining the advantages of Sequential Injection Analysis and batch analysers. The technique is highly versatile, enabling the automation of various liquid-liquid micro-extraction methods [2]. For the first time, we present a double-stage Lab-In-Syringe automated extraction procedure combining salting-out liquid-liquid extraction (SALLE) with on-line solid-phase extraction (SPE) coupled to high performance liquid chromatography (HPLC) [3]. In this work, we also demonstrated the compatibility of autosampler instruments with the stirring-assisted Lab-In-Syringe approach for automated sample preparation. The typically used multiposition selection valve was replaced by an autosampler allowing the aspiration of all reagent solutions and samples. The system was coupled on-line with LC for the subsequent separation of the sulfonamide antibiotics. The first step of the procedure was homogeneous liquid-liquid extraction using acetonitrile as an extraction solvent miscible with water and a saturated salt solution of magnesium sulfate and sodium chloride to induce phase separation. Sulfonamides were selected as model analytes with moderate polarity suitable for this technique. The advantage of the procedure is the compatibility of the solvent with HPLC. However, the achievable pre-concertation factor is relatively low. Therefore, we integrated a second step based on on-line SPE using the anion-exchange resin, which improved the analyte preconcentration and secondary clean-up.

Sulfonamides have an ampholytic character being neutral in a moderately acidic medium. Consequently, the SALLE procedure was carried out at pH 3. For anion exchange online SPE, the extract was diluted with ammonium buffer in-syringe to switch the pH to 10 before cartridge loading. Elution was then done by the acidic mobile phase of the HPLC.

The SPE cartridge was placed into the injection loop of the LC system. Analytes were eluted from the resin using an acidic HPLC mobile phase in gradient elution mode. The configuration enabled to perform a two-step, orthogonal, and automated extraction procedure in parallel with running analyte separation of the previous sample. This allowed shortening the effective time of the analysis to 13.5 min.

The developed system and methodology was successfully applied to sulfonamide determination in urine samples. Limits of detection ranged from 5.0 to 7.5 µg/L with confirmed linear working ranges up to 5,000 µg/L and RSD ≤ 5% (n=6) at a concentration level of 50 µg/L. Average recovery values were 102.7 ±7.4% for urine spiked with sulfonamides. Method optimization, including studies of SALLE and SPE preparation steps, mobile phase composition, and results from urine analysis, will be discussed.

Acknowledgements

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References

[1] F. Maya, J.M. Estela, V. Cerdà, Completely automated in-syringe dispersive liquid-liquid microextraction using solvents lighter than water, Anal. And Bioanal. Chemistry 402 (2012) 1383-1388.

[2] B. Horstkotte, P. Solich, The automation technique lab-in-syringe: a practical guide, Molecules 25 (2020) 1612.

[3] K. Fikarová, B. Horstkotte, D. Machián, H. Sklenářová, P. Solich, Lab-In-Syringe for automated double-stage sample preparation by coupling salting out liquid-liquid extraction with online solid-phase extraction and liquid chromatographic separation for sulfonamide antibiotics from urine, Talanta 221 (2021) 121427.

Fabric Phase Sorptive Extraction Followed by Gas Chromatography- Tandem Mass Spectrometry for the Analysis of Multiclass Fungicides in Water

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Keywords: *Environmental water monitoring, Fabric Phase Sorptive Extraction, Fungicides, Gas chromatography- tandem mass spectrometry,*

Fungicides are a type of pesticides usually used in viticulture to avoid fungi infection such as grey rot (*Botrytis cinerea*), mildew (*Plasmopara viti-cola*) and oidium (*Uncinula necator*) [1]. However, they can be primarily transported from agricultural fields to surface waters through surface runoff [2]. Indeed, in groundwater and superficial waters, these compounds are considered to pose a risk to the environment as well as to human health [3].
Before analysis, a sample preparation step for the extraction and concentration of analytes is required. Fabric Phase Sorptive Extraction (FPSE) is a technique, developed by Kabir and Furton, which employs a flexible and permeable fabric as the substrate chemically coated with a thin film hybrid inorganic-organic sorbent material via sol-gel technology. It offers simplicity, rapidity, low cost, and minimal solvent consumption.

A method based on FPSE as an efficient, green and simple alternative to other (micro)extraction techniques followed by gas chromatography-tandem mass spectrometry (GC-MS/MS) has been developed for the simultaneous analysis of fungicides in water. Some preliminary parameters were evaluated such as sol-gel sorbent coated FPSE membrane, desorption solvent, and solvent volume. The method was optimized applying an experimental design including the most critical parameters (i.e. sample volume, desorption solvent and time, NaCl addition and pH). In addition, it was validated showing good linearity and precision. Recoveries were studied at four fortification levels in five different water matrices obtaining satisfactory results. Finally, the developed method was applied for the extraction and preconcentration of fungicides in different water samples collected near viticulture zone. Eleven out of the seventeen studied fungicides were found in the analyzed samples.

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References

[1] R. M. González-Rodríguez, B. Cancho-Grande, J. Simal-Gandara. Multiresidue determination of 11 new fungicides in grapes and wines by liquid–liquid extraction/clean-up and programmable temperature vaporization injection with analyte protectants/gas chromatography/ion trap mass spectrometry. J. Chromatogr. A, 1216 (2009), 6033-6042.
[2] M. Celeiro, L. Vazquez, P. Nurerk, A. Kabir, A.G. Furton, T. Dagnac, M. Llompart. Fabric phase sorptive extraction for the determination of 17 multiclass fungicides in environmental water by gas chromatography-tandem mass spectrometry. J.Sep. Sci., 43 (2020), 1817-1829.
[3] M. Celeiro, R. Facorro, T. Dagnac, M. Llompart. Simultaneous determination of trace levels of fungicides in natural waters by solid-phase microextraction-gas chromatography-tandem mass spectrometry, Anal. Chim. Acta, 1020 (2018) 51-61.

Menthol-Based Deep Eutectic Solvent Dispersive Liquid-Liquid Microextraction: A Simple and Quick Approach for the Analysis Extraction of Phthalic Acid Esters from Water, Beverages and Infusions

O-21

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Keywords: *Dispersive liquid−liquid microextraction, high-performance liquid chromatography, menthol, natural deep eutectic solvent, phthalic acid esters.*

In recent years, interest in the use of deep eutectic solvents (DESs) in extraction techniques has increased notably, since a large number of them have low or negligible toxicity, presenting themselves as an environmentally friendly alternative to conventional solvents. In particular, DESs from natural products (natural DESs, NADESs) have aroused great interest. Up to now, most of the proposed DESs have been hydrophilic and their application to the extraction of hydrophobic analytes has been limited. Therefore, it is necessary to introduce new hydrophobic DESs, such as those based on menthol, which are characterized by their low toxicity and high biodegradability [1].

In this work, a NADES composed of L-menthol:acetic acid 1:1 (molar ratio) has been used for the first time in dispersive liquid-liquid microextraction (DLLME) to carry out the extraction of nine phthalic acid esters (PAEs) (i.e., dipropyl phthalate, butyl benzyl phthalate, dibutyl phthalate, diisopentyl phthalate, di-n-pentyl phthalate, dicyclohexyl phthalate di(2-ethylhexyl) phthalate, diisononyl phthalate, and diisodecyl phthalate) from tap and mineral water, as well as from different beverages (apple juice and soft drinks) and infusions, using dihexyl phthalate and di-n-octyl phthalate as internal standards [2]. PAEs have been widely used as plasticizers, many of which can have serious effects on health and the environment. For the determination of these analytes, high-performance liquid chromatography (HPLC) coupled to an UV detector was used, obtaining relative recovery values in the range 71-120 % and relative standard deviation (RSD) values less than or equal to 20 % for all the analytes in the different matrices analyzed. The limits of quantification of the method were between 3.5-51.1 μg/L.

Infrared spectroscopy and differential scanning calorimetry analyses of the DES drop after the DLLME procedure were carried out, observing the presence of an L-menthol-rich phase instead of the DES, which indicated that an important transference of acetic acid to the aqueous phase took place. Although the possibility of using L-menthol alone as extractant could be considered, with a previous thermal solubilization, non-quantitative extraction of the selected PAEs was achieved. Besides, extraction tests were also developed with thermal solubilized L-menthol adding another acid like HCl. Results suggested that DES extraction capacity is due to a "transient network" caused by the medium acidity, regardless of the type of acid used. This new NADES-based DLLME procedure demonstrated to be effective, quick and simple, as well as environmentally friendly, since relatively low toxic and biodegradable DES components were used [2].

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References

[1] I. Pacheco-Fernández, V. Pino, Green solvents in analytical chemistry, Curr. Opin. Green Sustain. Chem. 18 (2019) 42-50.

[2] C. Ortega-Zamora, J. González-Sálamo, C. Hernández-Sánchez, J. Hernandez-Borges, Menthol-based deep eutectic solvent dispersive liquid-liquid microextraction: A simple and quick approach for the analysis of phthalic acid esters from water and beverage samples, ACS Sustainable Chem. Eng. 8 (2020) 8783-8794.

Fabric Phase Sorptive Extraction: A Convenient Tool for Therapeutic Drug Monitoring, Illicit Drug Investigation and Other Clinical/Toxicological Study Using Unconventional Biological Fluids

O-22

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Keywords: *bioanalytical, clinical/toxicological investigation, Fabric Phase Sorptive Extraction, forensic applications, TDM*

Sample preparation has been recognized as a major step in the chemical analysis workflow. As such, substantial efforts have been invested in recent years to simplify the overall sample preparation process. Major focusses of these efforts include, miniaturization of the extraction device; minimizing/eliminating toxic and hazardous organic solvent consumption; eliminating sample pre-treatment and post-treatment steps; reducing the sample volume requirement; reducing extraction equilibrium time, maximizing extraction efficiency etc.

The extreme complexity of biological samples such as whole blood, plasma, serum, urine, and saliva demands a simple, fast and robust sample preparation process prior to the instrumental analysis. Conventional sorbent-based sample preparation techniques including solid phase extraction and its different modifications often involve protein precipitation, solvent evaporation and sample reconstitution as the integral part of sample preparation workflow. These extra steps are time consuming and may lead to substantial analyte loss. In order to eliminate these steps from the sample preparation workflow, in this presentation we will report the latest and innovative application of fabric phase sorptive extraction (FPSE) to small drugs analyses in different biological matrices like whole blood, plasma, urine, saliva, exhaled breath aerosol [1-3] with primary emphasis on unconventional sample matrix such as saliva due to its easy and non-invasive collection potential.

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References

[1] A. Kabir, K.G. Furton, N. Tinari, L. Grossi, D. Innosa, D. Macerola, A. Tartaglia, V. Di Donato, C. D'Ovidio, M. Locatelli, Fabric Phase Sorptive Extraction-High Performance Liquid Chromatography-Photo Diode Array Detection Method for Simultaneous Monitoring of Three Inflammatory Bowel Disease Treatment Drugs in Whole Blood, Plasma and Urine, J. Chromatogr. B, 1084 (2018) 53-63.
[2] A. Tartaglia, A. Kabir, F. D'Ambrosio, P. Ramundo, S. Ulusoy, H.I. Ulusoy, G.M. Merone, F. Savini, C. D'Ovidio, U. De Grazia, K.G. Furton, M. Locatelli, Fast *off-line* FPSE-HPLC-PDA determination of six NSAIDs in saliva samples, J. Chromatogr. B 1144 (2020) 122082.
[3] M. Locatelli, A. Tartaglia, H.I. Ulusoy, S. Ulusoy, F. Savini, S. Rossi, F. Santavenere, G.M. Merone, E. Bassotti, C. D'Ovidio, E. Rosato, K.G. Furton, A. Kabir, Fabric phase sorptive membrane array as non-invasive in vivo sampling device for human exposure to different compounds, Anal. Chem. 2021, in press, doi: 10.1021/acs.analchem.0c04663.

Electromembrane Extraction Using Deep Eutectic Solvents As Liquid Membrane

O-23

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Keywords: *Deep eutectic solvents, electromembrane extraction, green chemistry.*

Deep eutectic solvents (DESs) are currently emerging as a new class of green solvents, being inexpensive and environmentally friendly [1]. The solvents are composed of two (or more) solid components that can form intermolecular hydrogen bonds with each other, which results in a reduced melting point of the mixture to below or far below room temperature. This feature allows incorporation of components with different properties and chemical interactions, while maintaining a liquid state. DESs thus have potential as designer solvents. Electromembrane extraction (EME) is a microextraction technique where charged substances are extracted across a supported liquid membrane (SLM) and into a clean acceptor solution, assisted by an electric field [2]. Selectivity of extraction is largely determined by the SLM solvent, and DESs are therefore an interesting platform for designing task-specific SLM solvents for tuning extraction selectivity [3].

The presentation will feature an initial evaluation of selected hydrophobic DESs for EME of various model substances with different properties. The method was principally very green since only 4 µL DES was used per sample. Extraction efficiency related to molecular interactions, LC-MS compatibility, and advantages/disadvantages of DES-based EME will additionally be discussed.

References

[1] P. Makoś, E. Słupek, and J. Gębicki, Hydrophobic deep eutectic solvents in microextraction techniques–A review. Microchem. J. 152 (2020) 104384.

[2] S. Pedersen-Bjergaard and K.E. Rasmussen, Electrokinetic migration across artificial liquid membranes: New concept for rapid sample preparation of biological fluids. J. Chromatogr. A. 1109 (2) (2006) 183-190.

[3] F.A. Hansen, E. Santigosa-Murillo, M. Ramos-Payán, M. Muñoz, E. Leere Øiestad, and S. Pedersen-Bjergaard, Electromembrane extraction using deep eutectic solvents as the liquid membrane. Anal. Chim. Acta. 1143 (2021) 109-116.

Sample Introduction and Multidimensionality as Part of Sample Preparation

O-24

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Keywords: *Multi-cumulative trapping HS-SPME, LC-GC×GC, sample introduction, sample preparation*

Over the years, the advancements in the field of sample preparation towards more efficient, automated, and miniaturized techniques have been extraordinary. In this scenario, sample introduction and analysis dimensionality play an important role in the sample preparation protocol as well. The main goal is to extract and isolate the target analytes most efficiently, limiting losses and artifact formation.

Different sample introductions will be examined to evaluate their contribution to the overall sample preparation procedure. The liquid injection will be the starting point of this overview, pinpointing in particular to the selection of a proper liner (a parameter often overlooked). The excursus will continue with the headspace analysis and the use of a novel automated multi-cumulative trapping approach, novel advancement in the sample introduction will be discussed to emphasize how a wise optimization of these parameters can enhance the level of information acquired on the samples. Finally, a more sophisticated hyphenated system (LC-GCxGC) will be present to discuss the role of liquid chromatography as sample preparation step and of multidimensionality in the overall procedure.

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Automatization and Miniaturization of Sample Preparation of Food and Biological Samples for Lipidomics Studies

O-25

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Keywords: *Lipidomics, Automatization, LC-MS, GC-MS*

Lipidomics is the metabolomics branch that studies lipids within a living system. The classical approach in lipidomics analysis is based on the dismantling of the more complex lipidic molecules into their fatty acid constituents, that can be easily identified through Gas Chromatography coupled to Mass Spectrometry (GC-MS), in which the combination/complementarity of Linear Retention Index (LRI) and Electron Ionization (EI) data makes the identification process easy, automatic and reliable. Recently, the lipidomics approach opened new insight toward the determination of the native lipid composition. In fact, monitoring intact lipids can reflect more deeply the regulation of lipid metabolism in response to exogenous stimuli and provide elucidations on the perturbation of essential metabolic processes in which each species is involved. Ultra-high performance liquid chromatography coupled to mass spectrometry (UHPLC-MS) represents the technique of choice for the study of intact lipids. Nevertheless, achieving a fast, exhaustive and reliable identification is still a challenge, due to the not repeatable and poorly informative nature of atmospheric pressure ionization (API) MS techniques, normally hyphenated to LC, that avoid the building and the widespread use of LC-MS databases. In both cases a sample preparation step is required for the extraction and concentration of the target analytes. Those steps largely determines the quality of the results obtained and are the main source of systematic errors and random lack of precision of analytical methodologies. Moreover, traditional sample preparation techniques are also costly, time-consuming and generally labor-intensive, and furthermore, these techniques required high solvent content, which generates waste and is a main source of sample contamination. In this work we took advantage of fully automated preparative stations able to perform the extraction and the trans-esterification (for the GC analysis) of the lipid fraction obtained from both food and biological samples, prior to the injection into the UHPLC and GC instrumental setup, respectively. The use of robotic systems increased the reproducibility of the analysis, reduced the amount of solvents and minimized the errors due to the handling of the samples by the operators.

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Automated Analysis of 2-, 3-MCPD and Glycidyl Esters in Edible Oils and Fats

O-26

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***Keywords:** automation, MCPD esters, glycidyl esters, edible oils and fats*

3-Monochloropropane-1,2-diol (3-MCPD), 2-monochloropropane-1,3-diol (2-MCPD) and glycidol under the form of esters of different fatty acids are known processing contaminants formed during refining of oils and fats including the deodorisation step. 3-MCPD is classified as a possible human carcinogen while glycidol is known to be genotoxic and carcinogenic. Therefore, accurate quantification of these compounds in edible oils and fats is crucial to ensure food safety and to help evaluate human exposure to these contaminants. The analysis of these contaminants can be performed indirectly according to the official AOCS methods (AOCS Cd 29a-13, Cd 29b-13, Cd 29c-13) and more recently according to the Zwagerman-Overman method [1]. This method is gaining in popularity because it allows fast analysis of the 3 contaminants in one single method unlike the case with for example method AOCS Cd 29c-13. However, manual preparation of the samples according to this method is labour intensive, reaction times are critical for correct quantification of glycidol and to obtain good reproducibility. So, the method is more prone to human error, and the used reagents are harmful. Therefore, automation is of utmost importance for routine use in the fat and oil industries.

The present work describes a fully automated method for determination of 2-, 3-MCPD and glycidol in edible fats and oils based on the indirect Zwagerman-Overman method. The method is based on the fast alkaline transesterification and analysis of the phenyl boronic derivates by GC-MS/MS. An additional step has been integrated in the automated sample preparation method to remove more efficiently the excess of derivatising agent. This results in a more robust system ensuring less downtime related to source clean-up or column/pre-column exchange. Automation for real samples includes the preparation of a full calibration curve (9 levels and a blank). The only manual step in the method is placing a vial with the sample on the autosampler. Limits of detection in the low range of µg/kg were obtained for 2- and 3-MCPD and glycidol with recoveries in the range between 92 – 105%. Repeatability of the whole sample preparation procedure and analysis ranged below 6% (n=6). The proposed automated method offers additionally the advantage of adding at any time urgent samples which is of great importance in quality control laboratories for product release.

References

[1] R. Zwagerman, P. Overman, Optimized analysis of MCPD- and Glycidyl esters in edible oils and fats using fast alkaline transesterification and 13C-correction for glycidol overestimation: Validation including interlaboratory comparison, Eu. J. Lipid Sci. Technol. 121 (2019) 1800395.

Aroma Discovery of Low-cost to Luxury Honey Using a High-Capacity Sorptive Extraction Technique (HiSorb) and Gas Chromatography Mass Spectrometry

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Keywords: *Automation; Food authenticity; Food safety; Sample Preparation; Trace Analysis*

Honey is sold on a global scale and the market can be largely influenced by increasing concerns over product quality and authenticity. Volatile organic compounds (VOCs) are responsible for the aroma of this natural product, providing characteristic aromatic bouquets. The combined effect of several factors contributes to the distinct aromas, namely climate conditions, geographical location of production, flower nectar composition and post-harvest processes. The VOCs identified range both in compound class and molecular weight, with some key distinguishing compounds being present at low levels, making the analytical process challenging and time spent data processing laborious.

Here we demonstrate a simple, solvent-free method for fingerprinting different honey qualities through fully-automated sample extraction and enrichment by a high-capacity sorptive extraction technique (HiSorb), coupled to Gas Chromatography Mass Spectrometry. Data mining and chemometrics are combined into one easy-to-use platform, for rapid identification of key differences between the VOC profiles.

By identifying unique signatures amongst shared ubiquitous VOCs, we will show how this helps to distinguish between commercial low-cost to luxury brands and locally produced honey.

Determination of 2-Methyisoborneol and Geosmin as Malodours in Catfish for Quality Control Using a Fully Automated Sample Prep Platform Coupled with Gas Chromatography and Mass Spectrometry

O-28

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Keywords: *Automation; Food quality; Food science; Sample Preparation; Trace Analysis*

Accumulation of off-flavours and odours in fish flesh are a major contributor towards a decrease in fish meat quality because of the dislike by consumers. This is typically caused by two compounds, geosmin (GM) and 2-methylisoborneol (2-MIB), produced as secondary by-products of bacterial metabolism in water. These compounds have very low human sensory detection limits (or odour thresholds), which means that they can be present at trace-levels and still be detected with a human nose. Due to the lipophilic properties of these compounds their extraction from the fish tissue and subsequent analysis can be hindered due to simultaneous extraction of other volatile organic compounds (VOCs) which are present at much higher concentration levels. Lengthy extraction techniques such as steam distillation are typically required to extract the target compounds from the other VOCs present, producing cleaner chromatography. However, this is time consuming and manually labour-intensive for the analyst.

Here we demonstrate a simple, solvent-free and fully-automated technique using high-capacity sorptive extraction (HiSorb) coupled with Gas Chromatography and Mass Spectrometry for the identification of GM and 2-MIB at ppt-levels (pg/g) in catfish samples. The ‘prep-ahead’ functionality of the extraction and enrichment platform, Centri, provided enhanced sample management for increased sample throughput without compromising analytical sensitivity.

Development of a Low-Cost, Lab-Made Y-Interface for LC-GC Coupling for On-line Analysis in a Fully Automatized Way of Mineral Oils in Food Samples.

O-29

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Keywords: *Food analysis, Mineral oil hydrocarbons, Multidimensional liquid–gas chromatography;*

Consumers are daily exposed to a range of mineral oil hydrocarbons (MOH) via food. Major sources of MOH in food are food packaging and additives, processing aids, and lubricants. In 2019 an EU guidance was released covering specific directions for sampling and analysis of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) in food and FCM in the frame of Recommendation (EU) 2017/84 for the monitoring of mineral oils. The parameters required by the guide are increasingly stringent and coping with this type of analysis becomes more and more challenging. The topic of this lecture is to face the most important parameters required by the Recommendation, combining liquid chromatography to gas chromatography, using a lab-made LC-GC interface base on the Y-interface developed by Biedermann and Grob [1]. The response ratios of alkanes comprised between C10 and C50 were measured and were comprised between 0.9 and 1.1, with a maximum coefficient of variation of 4% (n = 5). Intermediate precision was evaluated for the fat/oil category along a period of 48 days obtaining a value of 10%. Seventeen different foods were analyzed in order to cover the categories reported in the EU guide. Saturated hydrocarbon contamination was detected only in a few samples (in the range 1-153 ppm); MOAH contamination was found only in one sample (sunflower oil: 15 ppm).

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References

[1] M. Biedermann, K. Grob, Memory effects with the on-column interface for on-line coupled high performance liquid chromatography-gas chromatography: The Y-interface, J. Chromatogr. A 1216 (2009) 8652–8658.

3D-printed Stirring Cages for Semi-Dispersive Fibrous Sorbent Extraction of Bisphenols

O-30

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Keywords: *3D printing, magnetic stirring devices, nanofibers, bisphenols, liquid chromatography*

Bisphenols are common precursors in the production of plastics and polymer resins as well as used plasticizers in the modification of their physical properties. Due to their massive utilization and potential leaching out of the plastic, bisphenols, above all bisphenol A, are ubiquitous in the environment. They count as quasi-persistent expressing that despite their degradability under UV radiation their concentration level is unlikely to decay due to permanent reinstatement. The problematic of bisphenols is due to their action as endocrine disruptors and, for some analogues, cytotoxicity and genotoxicity. Bisphenols A, AF, AP, BP, C, G, M, S, and Z were the subject of the present study.

Solid phase extraction (SPE) is one of the most used methodologies for sample clean-up and preconcentration in analytical determinations of environmental contaminants. Therefore, the investigation of novel sorbents for SPE showing alternative retention mechanisms or physical-chemical characteristics is a mayor focus in the area of analytical chemistry.

Recently, nanofibers have proven to be a versatile sorbent material due to their large surface to volume ratio, tuneable chemistry, and various modes how to handle them [1]. Among these reports, online coating for surface enlargement and functionalization as well as using them as restricted access materials can be found [2,3].

Nanofibers are mostly employed in column or cartridge format, yet excessive or insufficient fibre compaction can cause backpressure problems or channelling effect, respectively, as nanofibers do not show the required rigidity nor genuinely stable pores such as silica materials. Alternatively, they can be used as sorbent disc, yet the capacity is consequently limited [4].

Here, we present the outcomes of a recent work where we proposed a third handling method, that is using nanofibers to produce magnetic stirring devices that enable dispersive SPE. In this study we therefore aimed for a new approach of handling nanofibers for SPE procedures [5].

For this purpose, 3D-printing was exploited to fabricate cage-like holders for the nanofibrous sorbent that integrated a magnetic stirring bar. In these, small wads of fibres were tumbled similarly to clothing in a washing machine. The final device was placed into 100 mL of water sample and let stir until analytes were extracted (50 min), then rinsed with water, and finally placed into methanol for analyte desorption. The extract was then submitted to HPLC for analyte separation.

The cage-like design allowed us to take advantage of the lacking stiffness but high robustness of the fibrous sorbent material. High reproducibility of the extraction process and high analyte recoveries were obtained. With a preconcentration factor of 20, limits of detection of 0.2 ppb to 0.9 ppb were achieved, comparable to or better than previously reported methods.

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References

[1] M. Háková, L. Chocholoušová Havlíková, F. Švec, P.Solich, D. Šatínský, Electrospun nanofiber polymers as extraction phases in analytical chemistry – The advances of the last decade, TrAC Trends Anal. Chem. 110 (2019) 81-96.

[2] M. Háková, P. Chocholouš, A. Valachovič, J. Erben, J. Chvojka, P.Solich, F. Švec, D. Šatínský, On-line polydopamine coating as a new way to functionalize polypropylene fiber sorbent for solid phase extraction, Talanta 219 (2020) 121189.

[3] H. Raabová, M. Háková, L. Chocholoušová Havlíková, J. Erben, J. Chvojka, P. Solich, F. Švec, D. Šatínský, Poly-ε-caprolactone Nanofibrous Polymers: A Simple Alternative to Restricted Access Media for Extraction of Small Molecules from Biological Matrixes, Anal. Chem. 925 (2020) 6801-6805.

[4] I.H. Šrámková, L. Carbonell Rozas, B. Horstkotte, M. Háková, J. Erben, J. Chvojka, F. Švec, P. Solich, A. García-Campaña, D. Šatínský, Screening of extraction properties of nanofibers in a sequential injection analysis system using a 3D printed device, Talanta 197 (2019) 517-521.

[5] I.H. Šrámková, B. Horstkotte, J. Erben, J. Chvojka, F. Švec, P. Solich, D. Šatínský, 3D-Printed Magnetic Stirring Cages for Semidispersive Extraction of Bisphenols from Water Using Polymer Micro- and Nanofibers, Anal. Chem. 92 (2020) 3964-3971.

Automation of Immunoaffinity Extraction Using the Bead Injection Concept

O-31

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Keywords: *Bead Injection, Lab-on-valve, Antibody, Immunoaffinity*

Affinity separations are based on the interaction between specific immobilized ligands and target antibody, antigen, and/or protein. Different available ligands, such as proteins A and G, can be used to separate antibodies or their Fab fragments. Similarly, antigens can be isolated by immunoaffinity extraction using immobilized antibodies. In this context, the bead injection concept can be extremely useful for automation of immunoaffinity-based separation.

The bead injection concept comprises the injection and transport of particles inside a flow system. The particles can be made of different materials (polymers, silica) and decorated with chemical (chromophores, surface modifiers) or biochemical (enzymes, antibodies) structures. Sample treatment and/or analysis are implemented in lab-on-valve (LOV) devices, which are based on a monolithic structure with microconduits machined in a polymeric block, mounted atop a multiposition selection valve. Due to the mesofluidic scale of these channels, LOV systems present more potential and compatibility with real-world samples when compared to microfluidic devices [1]. The bead injection approach provides a fresh portion of sorbent, avoiding carry-over effects between samples and sorbent fouling from matrix components. Moreover, automation of column assembly provides repeatable packing of sorbent, with strict control of the flow rates applied during analyte retention and elution steps, contributing to acceptable results with significant reduction of sorbent amount.

In the present communication, the automation of solid-phase extraction based on immunoaffinity will be featured. The BI-LOV application includes in-situ biomolecule detection (e.g. binding assays) and sample pre-treatment using affinity capture coupled to different detection systems, such as mass spectrometry. The coupling of LOV with BI permits the establishment of immunoassays under different formats (e.g. sandwich and direct competitive ELISA and immunoaffinity chromatography), with real time monitoring of reaction(s) directly on the solid support surface. These methods require minimal operator intervention and short time-to-result intervals. They allow for a high surface-to-volume ratio, they require low amounts of sample, sorbent, and reagents, while preventing fouling phenomena

Several examples will be critically discussed, including the assessment of IgG capture in immobilized protein A through automated BI-LOV with in situ spectrophotometric quantification [2]. The miniaturization and automation of ELISA protocols will also be discussed, as a significant reduction on time-to-result is attained (2 h to 5 min) for carbamazepine and IgG quantification [3, 4].

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References

[1] M. Miró, H.M. Oliveira, M.A. Segundo, TrAC-Trends Anal. Chem. 30 (2011) 153-164.

[2] I.I. Ramos, S.S. Marques, L.M. Magalhães, L. Barreiros, S. Reis, J.L.F.C. Lima, M.A. Segundo, Talanta 204 (2019) 542-547.

[3] I.I. Ramos, P. Carl, R.J. Schneider, M.A. Segundo, Anal. Chim. Acta 1076 (2019) 91-99.

[4] I.I. Ramos, L.M. Magalhães, L. Barreiros, S. Reis, J.L.F.C. Lima, M.A. Segundo, Anal. Bioanal. Chem. 410 (2018) 981-988.

Combining Lab-In-Syringe with Bead-Injection for Preconcentration of Nonsteroidal Anti-Inflammatory Drugs in Surface Waters Coupled Online to High Performance Liquid Chromatography

O-32

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Keywords: *Bead-Injection, High performance liquid chromatography, Lab-In-Syringe, Nonsteroidal anti-inflammatory drugs, online coupling.*

Modern flow techniques have been versatile tools for the automation of sample preparation procedures directed to the determination of analytes in various matrices. In this work, a renewable micro-solid phase extraction method was developed combining for this purpose for the first time the automation techniques Lab-In-Syringe and Lab-On-Valve (LOV)[1]. This configuration of the flow system allowed analyte preconcentration of > millimeter sample volumes, as typically used in combination with commercial SPE cartridges, by enabling in-syringe mixing of sample and simultaneously, applying the bead-injection concept, i.e. handling sorbent particles as a suspension, in-situ renewable microcolumn formation was enabled in one of the LOV microchannel for μSPE using 4.4 mg of Oasis HLB sorbent (particle size of 30 μm).The preconcentration system was coupled online to a liquid chromatography for the quantification and determination of five nonsteroidal anti-inflammatory drugs(NSAIDs) ketoprofen, naproxen, flurbiprofen, diclofenac, and ibuprofen as model analytes of emerging environmental concern.

Method parameters such as loading and elution flow rates, sorbent suspension volume, and transfer volume were optimized. Analytes of interest were eluted using acetonitrile : water (50 : 50 % v/v) , loaded to online coupled HPLC, and separated on a Symmetry C18 column (4.6 x 150 mm, 5 µm) and C18 OPTI-GUARD® 1 mm guard column in isocratic regime using as mobile phase 30% (v/v) acetonitrile and 30%(v/v) methanol with 25 mmol/L ammonium formate buffer, pH 3.5. RSD values of 1% to 7% were obtained on a 20 µg/L concentration level with linear ranges of 10 µg/L to 200 µg/L and limit of detection in the range of 0.04 – 1.3 µg/L. This method was applied for the determination NSAIDs in surface water with recovery factors in the range of 91 to 109 % spiked at 20 µg/L level.

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References

[1] J. B. Quintana, M. Miró, J. M. Estela, and V. Cerdà, Automated On-Line Renewable Solid-Phase Extraction-Liquid Chromatography Exploiting Multisyringe Flow Injection-Bead Injection Lab-on-Valve Analysis, Anal. Chem. 78 (2006) 2832-2840.

Automated Monitoring in Sequential Injection Analysis

O-33

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Keywords: *automation, kinetic profile, sequential injection analysis, real-time monitoring*

Sequential injection analysis (SIA) can be easily applied to handle samples taken from different long-term processes in a dynamic mode together with on-line analysis in fully automated closed system. The main advantages of sample manipulation by SIA are (i) no need of human intervention in long-term process monitoring, (ii) real-time information concerning the monitored process, (iii) possibility to change tested conditions and to get insight into the effect of such modification without delay, (iv) recording detailed kinetic profiles, (v) possibility to connect several units to a single SIA system with time-controlled sampling from the respective units, and possible on-line connection to a separation step.

Applications of such monitoring from our research group involve monitoring dissolution/release of active substances from pharmaceutical formulations (including nanoparticles [1]) and release of active substances from nanofibers used as a support to deliver substances for therapeutic reasons on human skin in the area of pharmaceutical analysis. The other field relates to real-time monitoring interaction of a luminescent marker (single or in combination with inhibitors) with cell membrane transporters [2] in the field of toxicological/pharmacological studies. These studies are based on permeation testing while determining a fluorescent marker (Rhodamine 123) or a chemiluminescent marker in the form of secreted luciferase. To monitor such permeation tests a dedicated 3D printed module [3,4] was developed to improve method's sensitivity, to sample from both donor and acceptor compartments, and thus to get information concerning the real time marker concentration inside cells without the need of cell lysis.

The applications will be discussed in detail.

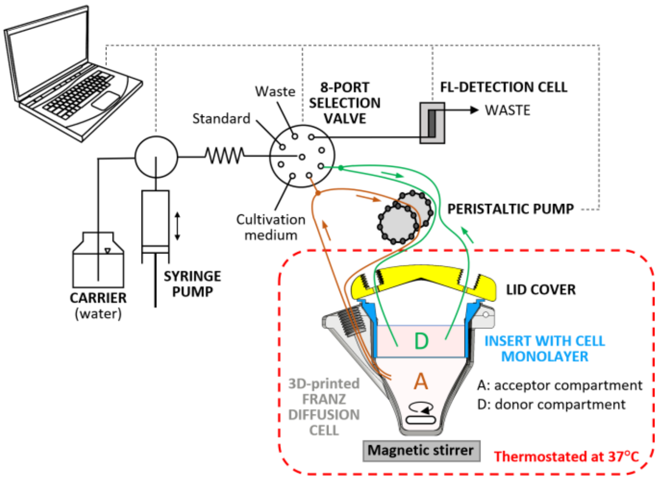

Figure 1. SIA system with 3D printed module for on-line monitoring interaction with cell membrane transporters [3].

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References

[1] A.C. Alves, I.I. Ramos, C. Nunes, L.M. Magalhaes, H. Sklenářová, M.A. Segundo, J.L.F.C. Lima, S. Reis, On-line automated evaluation of lipid nanoparticles transdermal permeation using Franz diffusion cell and low-pressure chromatography, Talanta 146 (2016) 369-374.

[2] L. Zelená, S.S. Marques, M.A. Segundo, M. Miró, P. Pávek, H. Sklenářová, P. Solich, Fully automatic flow-based device for monitoring of drug permeation across a cell monolayer, Anal. Bioanal. Chem. 408 (2016) 971-981.

[3] H. Sklenářová, M. Rosecká, B. Horstkotte, P. Pávek, M. Miró, P. Solich, 3D printed permeation module to monitor interaction of cell membrane transporters with exogenic compounds in real time, Anal. Chim. Acta, under submission, 2021.

[4] H. Sklenářová, P. Pávek. B. Horstkotte, P. Solich, M. Miró, Module for on-line monitoring of permeation tests, Czech patent application 2020-152.

Magnetic Dispersive Solid-Phase Extraction Using a Zeolite-Based Composite for Direct Electrochemical Determination of Lead(II) in Urine Using Screen-Printed Electrodes

O-34

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Keywords: *Gold nanostructured carbon electrode, Heavy metal, Magnetic composite, Urine samples, ZSM-5 zeolite*

A novel, simple, fast, sensitive and environmentally friendly approach is presented to determine lead in urine samples, combining magnetic dispersive solid-phase extraction (MDSPE) for sample preparation and screen-printed carbon electrodes (SPCEs) modified with gold nanoparticles for square-wave anodic stripping voltammetry [1]. This association involves the miniaturization of sample preparation and measurement process [1,2].

A zeolite-based magnetic composite (i.e., ZSM-5 zeolite/$Fe_2O_{3(tr)}$) was employed as an efficient sorbent, which combines the advantages of magnetic materials (e.g., easy manipulation under external magnetic field) with the remarkable properties of zeolites (e.g., high adsorption capacity, thermal and chemical stability, environmentally friendly, economical, simple modification to get the desired chemical and physical properties).

The sample preparation consist on, firstly, extracting lead directly from urine samples employing the ZSM-5/$Fe_2O_{3(tr)}$ composite, then, the composite enriched with lead was deposited onto a modified SPCE and finally covered with a suitable electrolyte for electrochemical detection. Thereby, the elution and detection of lead were carried out in a single step, which is the main contribution of this work. To optimize experimental parameters affecting MDSPE, a multivariate approach was employed. The method has been evaluated under optimized extraction conditions (i.e., type of sorbent, ZSM-5/$Fe_2O_{3(tr)}$; amount of sorbent, 10 mg; sample pH, 4.8; extraction time, 1 min; and HCl concentration, 1 M) using standard addition calibration. Standard addition calibration curves gave a good linearity in the range from 0 to 25 µg L^{-1} with correlation coefficients ranging from 0.992 to 0.998 (N=6). The limit of detection, evaluated empirically and statistically, ranged from 1.0 to 2.0 µg L^{-1} and from 0.8 to 1.6 µg L^{-1}, respectively, which are lower than the normal mean value of Pb (i.e., ~35 µg L^{-1}) found in the urine of people without evident occupational, medicinal, or other unusual sources of exposure [3]. The repeatability of the proposed method was evaluated obtaining coefficients of variation between 12 and 15% (n=6).

The method was used to analyze Pb(II)-spiked urine samples, and apparent recoveries ranged between 99 and 107%, with coefficients of variation of <20%. Therefore, this is a new and successful contribution to the portable total analytical systems.

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References

[1] E. Fernández, L. Vidal, J. Silvestre-Albero, A. Canals. Magnetic dispersive solid-phase extraction using a zeolite-based composite for direct electrochemical determination of lead(II) in urine using screen-printed electrodes, Microchim. Acta 187 (2020) 87.

[2] P. Baile, L. Vidal, A. Canals, Magnetic dispersive solid-phase extraction using ZSM-5 zeolite/Fe_2O_3 composite coupled with screen-printed electrodes based electrochemical detector for determination of cadmium in urine samples, Talanta 220 (2020) 121394.

[3] L.J. Goldwater, A.W. Hoover, N. Yuh, An international study of “Normal” levels of lead in blood and urine, Arch. Environ. Health. 15 (1967) 60–63.

Influence of Sampling Trap Materials on the Volatilome From *In Vitro* and *Ex Vivo* Samples

O-35

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***Keywords:** adsorbent tubes, breath, multidimensional chromatography, serum, thermal desorption.*

In this study, we evaluated and compared the sampling performance of different thermal desorption (TD) adsorbent materials, both in *in vitro* and *ex vivo* situations, in the context of clinically-relevant samples.
Growing indeed are the applications on VOCs from biological fluids (breath, serum etc), specially as possible biomarkers of specific disease states. Because of the wide variety of adsorbent materials, the tube can be filled with, it may be challenging to select the optimal tube for biological samples. Indeed, these trapping materials can be used alone or in combination, and depending on the characteristics (chemical and physical), the selectivity can be tuned, as well as the sensitivity and repeatability.

Specifically, we used 7 different adsorbents (Tenax TA, Tenax GR, Carbopack B, Carbopack 5TD, Carbopack 1016, Carbopack X and Sulphicarb), packed singularly and in combination, on Fetal Bovine Serum (FBS) and human breath spiked with probe analytes. For the evaluation, we selected a mix of 19 standards (probe analytes) to monitor and compare the sensitivity and repeatability between the different adsorbents.
In the *in vitro* sampling setup, spiked FBS was used to mimic the biological matrix, and a dynamic headspace extraction was performed. For the *ex vivo*, breath was collected in Tedlar bags in which standards were successively flash-vaporized. In both cases, after extraction, the tubes were thermally desorbed on a comprehensive two-dimensional gas chromatography system coupled to a time-of-flight mass spectrometer (GC×GC-TOF MS).
For both sample matrices and in the targeted analysis on the probe VOCs, the tubes packed with Tenax TA alone resulted the most sensitive with the highest repeatability, in the range of 2-22 RSD % for breath and 2-32 RSD % for serum analysis.

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References

[1] E. Woolfenden, Thermal Desorption for Gas Chromatography, in Gas Chromatography, Elsevier, 2012.
[2] F.A. Franchina, G. Purcaro, A. Burklund, M. Beccaria, J.E. Hill, Evaluation of different adsorbent materials for the untargeted and targeted bacterial VOC analysis using GC×GC-MS, Anal. Chim. Acta, 20 (2019) 146-153.
[3] F.A. Franchina, D. Zanella, E. Lazzari, P.H. Stefanuto, J.F. Focant, Investigating aroma diversity combining purge-and-trap, comprehensive two-dimensional gas chromatography, and mass spectrometry, J. Sep. Sci., 43 (2019) 1790-1799.

Fabric Phase Sorptive Membrane Array: A Novel Approach for Non-Invasive In Vivo Sampling for Disease Diagnosis, Air Pollution monitoring, and Beyond

O-36

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Keywords: *exhaled breath aerosol, Fabric Phase Sorptive Membrane, human exposure, HPLC-MS/MS, non-invasive sampling*

In recent years, increasing attention has been paid to the development of new technologies and innovative devices able to monitor, through *non-invasive* sampling, the levels of human exposure to different compounds present in the environment, as well as the evaluation of compound(s) that could be related to a specific disease. Exhaled breath aerosol (EBA) containing water molecules, volatile and non-volatile compounds, micro-drops and particles of biological origin that are extremely interesting in terms of analytical-clinical point of view as it is enriched with numerous metabolites/biomarker compounds, easily exploitable for diagnostic purposes. These compounds actually represent chemicals to which the subject is exposed (at an environmental level or following intake through diet or lifestyle habits), as well as the biomarker(s) pertaining to any specific disease condition [1]. The development of innovative technologies, like Fabric Phase Sorptive Membrane (FPSM) array, able to perform the sampling step through a non-invasive procedure, is utterly needed in order to increase the knowledge of the exposure to different chemicals.

In this presentation, this novel approach for non-invasive *in vivo* sampling for disease diagnosis, air pollution monitoring and beyond is presented for the first time and compared with other technologies currently in use. During the presentation, the advantages, disadvantages and limitations of all the procedures for this type of analysis will be highlighted. In this presentation, the different approaches will also be critically assessed based on the "*green*" profile characteristics of the procedures [2], both relating to sampling and subsequent instrumental analysis.

Acknowledgements

The authors thank MIUR ex 60%, "G. d'Annunzio" University of Chieti-Pescara (Italy) and the Department of Chemistry and Biochemistry, Florida International University for supporting the present work.

References

[1] M. Locatelli, A. Tartaglia, H.I. Ulusoy, S. Ulusoy, F. Savini, S. Rossi, F. Santavenere, G.M. Merone, E. Bassotti, C. D'Ovidio, E. Rosato, K.G. Furton, A. Kabir, Fabric phase sorptive membrane array as non-invasive in vivo sampling device for human exposure to different compounds, Anal. Chem. 2021, in press, doi: 10.1021/acs.analchem.0c04663.
[2] Płotka-Wasylka J, A new tool for the evaluation of the analytical procedure: Green Analytical Procedure Index, Talanta 181 (2018) 204–209.

Application of New HLB Solid Phase Extraction Towards Analysis of Pharmaceuticals in Plasma Samples

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Keywords: *bioanalysis, HLB, sample preparation,*

The use of Solid Phase Extraction (SPE) prior to LC-MS analysis is the established sample preparation technique to reduce matrix impurities in the samples in a resonable time and with minimum costs. Conceptually, during the SPE procedure analyte(s) are bound to the adsorbent while the matrix components are washed off. An HLB, hydrophilic-lipophilic balanced, polymeric sorbent enables extraction of a broad range of compounds from aqueous samples. The use of this polymeric sorbent offers unique advantages over traditional silica-based sorbents during SPE procedures. These include stability over a wider pH range, better flow rates, higher loading capacity, and preserving the performance during sorbent drying out to name a few.

An SPE procedure using a new HLB SPE cartridges was performed for extraction of 20-analytes from human plasma samples. The analytes represented multiple drug classes and had different hydrophobilicties and polarities. Effectiveness of the new HLB SPE was evaluated towards analyte reciveries and sample cleanliness. All the analytes had an absolute recovery between 80 to 120% using a standard 5 – step SPE procedure. Further, matrix effects in the final SPE-cleaned samples were evaluated and minimal to no ion suppression effects (<10%) were observed. These novel HLB cartridges offer the end-user confidence in obtaining less complex and cleaner samples for analysis.

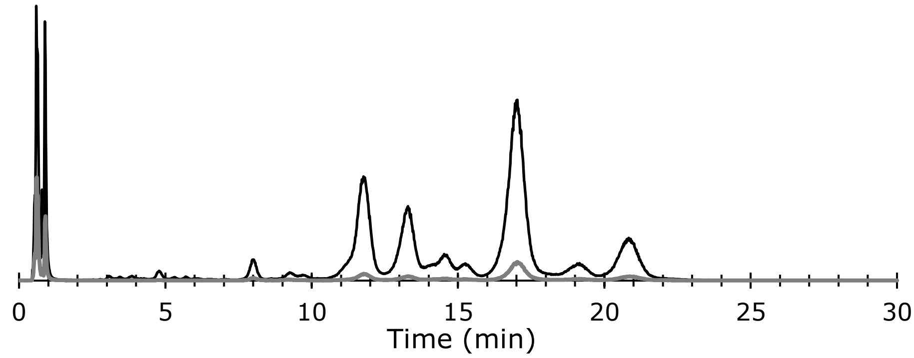

Figure 1. LC-MS/MS analysis of phospholipids in the SPE-cleaned samples of human plasma (grey) versus the protein-precipitated samples (black). More than 92% of phospholipids were removed by using SPE cleanup procedure.

Measurement of Protein Binding Property of Drugs Using High-Throughput Automated Solid Phase Microextraction and LC-MS/MS Detection

O-38

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Keywords: *bioanalysis, free fraction, protein binding, sample preparation, solid phase microextraction*

The use of Solid Phase Microextraction (SPME) has been widely accepted as fast and convenient sample preparation method. It has been applied to a wide range of samples and utilizes adsorbent-containing coated devices. In this work we have used the solid phase microextraction towards measurement of free fraction of pharmaceutical compounds in biological samples in the highly throughput manner using 96-well format compatible with automated robotic systems.
Protein binding is an important property of pharmaceutical compounds as only free fraction exert pharmacological effect. The developed extraction method using a novel BioSPME device allowed quantitative measurement of free analyte fraction of pharmaceutical drugs from plasma using LC-MS/MS detection. The manipulation of the BioSPME device during the extraction method was done using robotic grippers on Hamilton Starlet system. The protein binding accuracy of the proposed method was evaluated by comparison of the calculated values to these obtained using equilibrium dialysis method and the values found in scientific publications. The results of the protein binding measurements will be presented for compounds across the range of hydrophobicities, charges and molecular weights. The proposed sample preparation method provided high accuracy of the obtained protein binding values and was 3-times faster in comparison to the standard methodology.

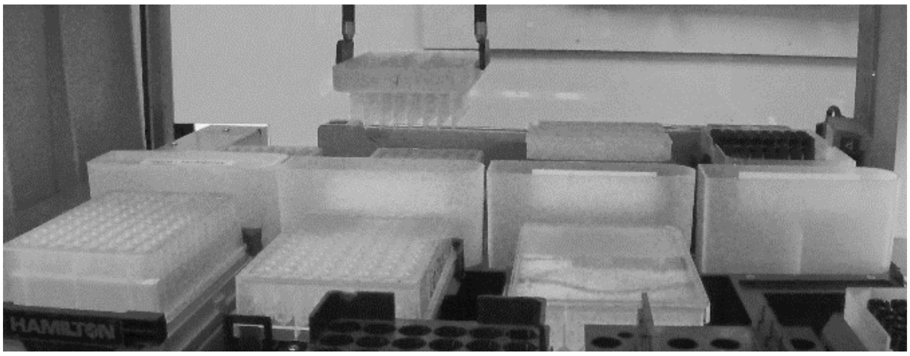

Figure 1. Manipulation of the 96-pin BioSPME device by Hamilton Starlet robot.

Matrix Modifiers to Improve SPME Performances for analytes Heavily Bound to Biological Samples

O-39

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Keywords: *Bioanalysis, Binding Matrix, Matrix Modifiers, SPME*

Solid-Phase Micro-Extraction (SPME) is a micro extraction technique developed in the early 90's by Arthur and Pawliszyn [1]. SPME allows for analyte isolation and enrichment, along with matrix cleanup, in a single sample preparation step. To achieve this simplicity, a small amount of extraction phase immobilized on a solid support is directly exposed to the sample. Then, the extraction occurs by partitioning of analytes among both phases. Noteworthy, the analytes are transported from the sample to the extraction phase via diffusion through the boundary layer, generated by the concentration gradient between phases. The phenomenon occurs until the system reaches equilibrium. The latter depends on the analyte partition coefficient, the volume of extraction phase, and the volume of sample. Furthermore, the partition coefficient will also change its magnitude when changes of temperature, solvent composition or ionic strength are observed. Nevertheless, these fundamental considerations are only valid for small molecules free in solution; a condition that not often is fulfilled in bioanalysis where the analytes are mostly bound to different macromolecules. In this regard, binding constants between the analyte and the macromolecules (binding matrix) are defined. It is important to highlight that the formed complex is characterized by a high molecular weight and very low diffusion coefficients, drastically limiting the extraction efficiency. Hence, the larger is the binding constant the lower is the extraction efficiency regardless of the distribution constant value. In this work, the authors present alternatives for matrix modification that aid the release of analytes from the matrix, decreasing the binding constants, without significantly compromising the distribution constant. As a result, the extraction efficiency can be improved up to an order of magnitude, enabling inconceivable applications such as determination of highly bound analytes from complex biological matrixes by direct immersion SPME. Among these alternatives, the first one consists in solvent addition, where two main examples are introduced. On the one hand, the effect of solvent addition on the recovery of immunosuppressive drugs from whole blood. Different solvents were evaluated finding acetonitrile (ACN) as the best option. It was demonstrated that low proportions of ACN promoted the release of analytes by denaturing the red blood cells without decreasing the partition coefficient [2,3]. More important, the denaturing and analyte release step was simultaneous with the extraction process. On the other hand, a group of twenty drugs from different families regulated by the World Anti Doping Agency (WADA) were determined from plasma by SPME. Solvent addition has demonstrated up to 5-fold increasing in sensitivity for the most heavily bound molecules such as diazepam, propranolol, and buprenorphine [4]. The second approach refers to the addition of aqueous modifiers that help the denaturing process of the macromolecules. To this end, additives such as zinc sulfate, guanidine, and trifluoroacetic at different concentrations and proportions were implemented. For immunosuppressive drugs determination from whole blood, zinc sulfate was explored. However, the high hydrophobicity of the compounds did not allow the effective release to the media, remaining in the precipitate of red blood cells [2,3]. Similarly, the effect of the sole addition of guanidine hydrochloride to plasma for endocannabinoids determination did not give positive results. Although the proteins were denatured, the coprecipitation of analytes was the predominant process [5]. Finally, the last option consisted in a combination of the first and second approach. As a result, in all applied cases the extraction performances were increased up to one order of magnitude. For instance, the addition of 1300 µL of the mixture 0.1M $ZnSO_4$:ACN:H_2O (60:30:10, v/v) to 200 µL of whole blood produced a 10-fold improvement on the LOQs for different SPME-MS determinations [2,3]. Similarly, the addition of 50 µL of guanidine hydrochloride (1 $mol \cdot L^{-1}$), 75 µL of ACN, and 75 µL of H_2O to 300 µL of plasma, obtaining an increased sensitivity between 5 and 8 times for the endocannabinoids studied [5]. To conclude, the original development considerably improves the LOQs for challenging applications in SPME analysis. Namely, highly nonpolar analytes heavily bound to macromolecules in a biological fluid. Also, it implements the concept of extraction during the analyte's release process. In this manner, the herein established concept boosts the high-throughput capabilities of any analytical method without compromising the sensitivity. A required feature for SPME-MS approaches that circumvent the time-consuming separation step.

Acknowledgements

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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] G.A. Gómez-Ríos, M. Tascon, N. Reyes-Garcés, E. Boyacı, J.J. Poole, J. Pawliszyn, Rapid determination of immunosuppressive drug concentrations in whole blood by coated blade spray-tandem mass spectrometry (CBS-MS/MS), Anal. Chim. Acta. 999 (2018) 69–75.

[3] M. Tascon, M.N. Alam, G.A. Gomez-Rios, J. Pawliszyn, Development of a microfluidic open interface with flow iso-lated desorption volume for the direct coupling of SPME de-vices to mass spectrometry, Anal. Chem. 90 (2018) 2631-2638.

[4] G.A. Gómez-Ríos, M. Tascon, N. Reyes-Garcés, J. Poole, E. Boyacı, J. Pawliszyn, Quantitative analysis of biofluid spots by coated blade spray mass spectrometry, a new approach to rapid screening, Sci. Rep. 7 (2017) 16104.

[5] V.R. Acquaro Junior, G.A. Goméz-Ríos, M. Tascon, M.E. Costa Queiroz, J. Pawliszyn, Analysis of endocannabinoids in plasma samples by biocompatible solid-phase microextraction devices coupled to mass spectrometry, Anal. Chim. Acta. 1091 (2019) 135–145.

Hollow-Fiber Supported Liquid Membranes And Molecularly Imprinted Polymers As Solid Acceptor Phase For Highly Selective Extractions

O-40

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Keywords: *Sample preparation; Molecularly imprinted polymers; Hollow-fiber; Liquid-phase microextraction*

Sample preparation is still considered the bottle-neck of the whole analytical process. Nowadays, several sample preparation techniques are available, however all of them suffer from a lack of the selectivity. At this regard, molecularly imprinted polymers (MIPs) are considered excellent materials able to perform selective extractions. Recently, new objectives in sample preparation have been set, including to use smaller initial sample sizes; to facilitate automation; and, to minimize the amount of glassware and organic solvents needed. MIP incorporation to other microextraction techniques offers a new strategy in order to fulfil current sample preparation requirements [1]. However, even using MIPs, the complexity of the sample can affect recoveries of target analytes, negatively affecting the analytical method precision and accuracy. The use of a porous membrane, as a protective sleeve, is one of the simplest approaches to circumvent the difficulties mentioned above in the analysis of complex and "dirty" samples. Accordingly, the different recent approaches developed in our lab combining hollow-fiber membranes and MIPs as a new highly selective microextraction technique will be presented. The advantages and drawbacks of this approach as well as the future expected trends will be discussed.

References

[1] A. Martín_Esteban, E. Turiel, Molecularly imprinted polymers-based microextraction techniques, Trends Anal. Chem. 118 (2019) 574-586.

Biofluid Sampler: Beginning of a New Era of Mail-in-Analysis of Whole Blood Sample

O-41

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Keywords: *biofluids sampler, whole blood, mail-in-analysis, TDM*

Among all the biofluids (blood, urine, saliva, sweat), whole blood is the most information rich as well as the most complex sample matrix. It provides a temporal snapshot of the body and reveals the overall physiological condition. Blood consists of ~55% aqueous fraction (plasma) and ~45% solid materials (formed elements). Although blood is the primary sample in most of the clinical chemistry-based investigations, due to the lack of available sample preparation technology that can handle whole blood directly, it is usually converted into plasma or serum prior the analysis. Exogenous substances in blood such as drugs, poisons, pollutants enter in the blood stream via different routes (food, water, inhalation, ingestion, etc.), undergo metabolism, and the residues remain in equilibrium between the liquid part (plasma) and the suspended solid particles (formed elements). When blood is converted into plasma, a significant loss of the exogenous analytes could occur. The concentration of analytes in plasma also remain in equilibrium between the aqueous solution and the dissolved proteins. As such, when plasma undergoes protein precipitation prior to deploying any extraction technique such as solid phase extraction, another round of analyte loss is practically inevitable.

Convenience in using, ability to handle whole blood, minimally invasive sample collection opportunity, and ability to ship the dried samples without expensive temperature control process and other advantages of DBS cards have catalyzed the exponential growth of this technique in numerous applications including newborn screening, toxicology, preclinical and clinical drug development, therapeutic drug monitoring (TDM), drug and sports doping screening, medical screening and nutrition in recent years.

Biofluid Sampler [1] and Sample Preparation device (BFS) is specifically designed to eliminate all major shortcomings of DBS cards and their different modifications in a rational scientific way. Advantages of BFSs include: (a) capable of retaining low to high sample volume (10–1000 µL); (b) each BFS is a separate sampling and sample preparation device, therefore hematocrit problem is not an issue in BFS (entire BFS is used for instrumental analysis, not a punched-out segment of the dried blood spot as in DBS cards); (c) spot homogeneity is not an issue in BFS as the entire device is exposed to back-extraction for analyte recovery; (d) the BFSs can be created in small size (1/4″) to big size (2″) depending on the sample volume requirement; (e) unlike DBS card which primarily utilize physical adsorption as the analyte retention mechanism, BFSs utilize a plethora of intermolecular interactions such as London dispersion, hydrogen bonding, dipole-dipole interaction, π- π stacking interaction; (f) sponge-like porous architecture of sol-gel sorbent coated on BFS allows rapid dissipation of the biofluid homogeneously throughout the device; (g) strong intermolecular interactions between the BFS and the biofluids minimizes the analyte loss during regular transportation and shipping; (h) when matrix interferents complicates the downstream separation, BFSs can be used as the extraction device.

The primary objectives of the current presentation is to describe the novel biofluid sampler for direct sampling of low to high volume of whole blood sample and to inform the audience as to how BFS may dramatically impact on the current practice of whole blood analysis for clinical/toxicological/forensic analysis.

Acknowledgements

The authors thank MIUR ex 60%, "G. d'Annunzio" University of Chieti-Pescara (Italy) and the Department of Chemistry and Biochemistry, Florida International University for supporting the present work.

References

[1] M. Locatelli, A. Tartaglia, F. D'Ambrosio, P. Ramundo, H.I. Ulusoy, K.G. Furton, A. Kabir, Biofluid sampler: A new gateway for mail-in-analysis of whole blood samples, J. Chromatogr. B 1143 (2020) 1-7.

Advances in Ionic Liquid-Based Sorbent Materials for Sample Preparation

O-42

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Keywords: *Ionic Liquids, Nucleic Acids, Chromatography, Solid-Phase Microextraction, Thin-Film Microextraction.*

Ionic liquids (ILs) can be designed to exhibit unique properties for their use in a number of applications in analytical and bioanalytical chemistry. This talk will focus on the design and synthesis of ILs, magnetic ionic liquids (MILs), and polymeric ionic liquids (PILs) as well as the use of these materials in a number of applications within sample preparation. Nucleic acids are biopolymers that constitute important diagnostic molecules for a broad range of applications from clinical testing to forensic analysis. A major challenge faced by DNA and RNA analysis techniques is the selective extraction of particular nucleic acid sequences using rapid and sensitive methodologies. It will be shown in this presentation that ion-tagged oligonucleotides (ITOs) can be used in conjunction with MILs to efficiently capture DNA sequences from complex samples. The ITOs can be created through thio-lene “click” chemistry and the nature of the ion tag can influence the partitioning of the ITO to the hydrophobic MIL. This novel liquid-phase approach towards sequence-selective DNA capture provides superior extraction efficiencies to conventional magnetic bead technology as well as a platform for using external fields to manipulate the liquid droplets. We will also discuss the use of PIL sorbent materials in both solid-phase microextraction (SPME) and thin-film microextraction (TFME) and the advantages that TFME offers in the rapid uptake and release of nucleic acids. Finally, we will discuss the coupling of microextraction methods with isothermal amplification to produce point-of-care diagnostic platforms that can be used in the field, such as demonstrated in Figure 1 for the rapid diagnosis of *Mycobacterium tuberculosis* using colorometric loop-mediated isothermal amplification.

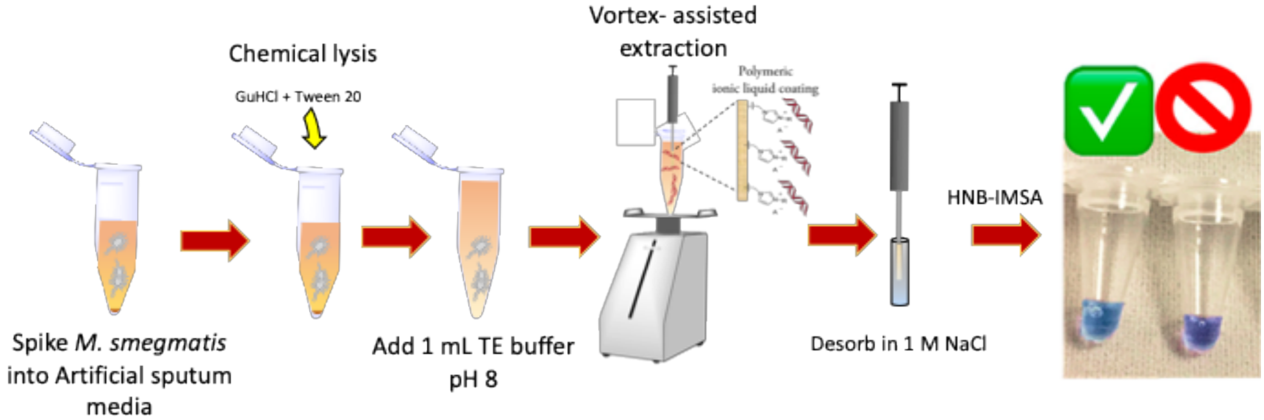

Figure 1. Protocol developed for the rapid extraction of nucleic acid from *Mycobacterium tuberculosis* using SPME coupled to colorimetric loop-mediated isothermal amplification.

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The authors acknowledge funding from the Chemical Measurement and Imaging Program at the National Science Foundation (Grant No. CHE-1709372).

"EuChemS Division of Green and Sustainable Chemistry/Compressed CO_2: An Attractive Green Solvent for the Preparation of Nanostructured Materials"

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Keywords: *Compressed gases, Biomedical applications, Green and Sustainable Chemistry, Nanostructured Materials*

During this lecture, the EuChemS Division of Green and Sustainable Chemistry (DGSC) will be presented. The potential of compressed CO2 on the preparation of nanostructured materials for biomedical applications will be briefly exposed, as one example of the type of activities done by scientists engaged in the DGSC.

The DGSC was formally announced at the opening ceremony of the 2nd EuCheMS congress on Green and Sustainable Chemistry (2EUGSC – Lisbon), in 2015. The DGSC is a constantly growing network of scientist dedicated to the advancement of sustainability and green chemistry in Europe. The Division organises numerous conferences, workshops, and supports widespread activities that foster multidisciplinary cross-fertilization of ideas in order to promote the advancement of Sustainability and Green Chemistry in Europe. The Division actively promotes teaching activities, for example the incorporation of the principles of Green Chemistry into the actual curriculum on the bachelor, master and doctoral levels either by modification of existing content or by creating new courses, modules or study areas. The Division also recognizes scientists that make an outstanding contribution to the development of green and sustainable chemistry by launching the biannual European Sustainable Chemistry Award (ESCA).

Nano- and micro-particulate molecular materials (micro- and nanocrystals, nanosuspensions, microemulsions, nanovesicles, polymeric particles, etc..) have gained a lot of attention for biomedical applications. Despite the potential of these materials, from which polymeric micro/nanoparticles and vesicles are the most thoroughly investigated, a high degree of structural homogeneity is crucial for their optimum performance as functional entities. However, the achievement of homogeneous nanostructured materials with high batch to batch reproducibility is not an easy issue. The method of preparation plays a crucial role in this degree of heterogeneity and therefore, methods that allow a well controlled nanostructuring, not only regarding size but also morphology and supramolecular organization, are necessary. The scalability of such preparation processes is a usually forgotten issue. However, this aspect is also of high relevance for commercially exploiting the potential of nanomaterials for biomedical applications, which fulfill standardization and quality requirements requested by regulatory agencies.

Since conventional precipitation processes usually present difficulties in controlling a homogeneous assembling of the molecules present in a bulk system, especially when scaling-up, "down-stream" operations, such as milling in the case of particles and extrusion or sonication for vesicles, are necessary in order to achieve or isolate the desired structures.

Compressed fluids (CFs), like compressed CO_2, have a great deal of promise as green solvent media for material processing, since their unique characteristics between those of liquid and gases, allow the achievement of materials presenting highly homogeneous structure [1]. In this lecture will be shown part of the work carried out in our lab related to the use of green compressed CO_2 for the preparation of more homogeneous crystalline and non-crystalline ordered materials for biomedical applications [2-5].

References

[1] J.D. Holmes, K.P. Johnston, R.C. Doty, B.A. Korgel, Control of Thickness and Orientation of Solution-Grown Silicon Nanowires, Science *287* (2000) 1471.

[2] S. Sala, A. Córdoba, E. Moreno-Calvo, E. Elizondo, M. Muntó, P.E. Rojas, M.À. Larrayoz, N. Ventosa, J. Veciana, Crystallization of Microparticulate Pure Polymorphs of Active Pharmaceutical Ingredients Using CO2-Expanded Solvents, Cryst. Growth Des. 12 (2012), 1717-1726.

[3] E. Elizondo, J. Larsen, N.S. Hatzakis, I. Cabrera, T. Bjørnholm, J. Veciana, D. Stamou, N. Ventosa, Influence of the Preparation Route on the Supramolecular Organization of Lipids in a Vesicular System, J. Am. Chem. Soc. 134 (2012) 1918–1921.

[4] I. Cabrera, E. Elizondo, O. Esteban, J.L. Corchero, M. Melgarejo, D. Pulido, A. Córdoba, E. Moreno, U. Unzueta, E. Vazquez, I. Abasolo, S. Schwartz, A. Villaverde, F. Albericio, M. Royo, M.F. García-Parajo, N. Ventosa, J. Veciana, Multifunctional Nanovesicle-Bioactive Conjugates Prepared by a One-Step Scalable Method Using CO2-Expanded Solvents, *Nano Lett.* 13 (2013) 3766–37745.

[5] I. Cabrerar, I. Abasolo, J.L. Corchero, E. Elizondo, P.R. Gil, E. Moreno, J. Faraudo, S. Sala, D. Bueno, E. González-Mira, M. Rivas, M. Melgarejo, D. Pulido, F. Albericio, M. Royo, A. Villaverde, M.F. García-Parajo, S. Schwartz, N. Ventosa, J. Veciana, α-Galactosidase-A Loaded-Nanoliposomes with Enhanced Enzymatic Activity and Intracellular Penetration, Adv. Health. Mater. 5 (2016) 829-840.

Acknowledgements

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07. Abstracts of posters

Capsule Phase Microextraction of Selected Polycyclic Aromatic Hydrocarbons from Water Samples Prior to their Determination by GC-MS

P-1

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Keywords: *Polycyclic aromatic hydrocarbons,* capsule phase microextraction*, GC-MS*

Capsule phase microextraction (CPME) is a green sample preparation technique that integrates the filtration and stirring mechanism into a single extraction device. In this study, CPME was employed for the extraction of four selected polycyclic aromatic hydrocarbons (naphthalene, fluorene, phenanthrene and pyrene) from water samples prior to their determination by gas chromatography-mass spectrometry. Phenanthrene and pyrene have been detected at the highest concentrations in drinking water [1], while all of the selected PAHs are expected to be present in environmental water samples [2]. In order to find the optimum adsorbent, multiple sol-gel hybrid CPME media were evaluated and the highest extraction efficiency was observed with the sol-gel poly(caprolactone)-poly(dimethylsiloxane)-poly(caprolactone) capsules. Accordingly, the main parameters affecting the steps of the CPME procedure were optimized. Under optimum conditions, limits of detection ranged between 0.03-0.07 ng mL^{-1}. The relative standard deviation for the within-day and between-days repeatability were lower than 7.7% and 8.5%, respectively. The method was successfully applied to the analysis of tap water, mineral water and lake water samples. It was observed that the developed CPME method could efficiently simplify the overall sample preparation protocol, since it overcomes the need for sample filtration prior to the extraction and the solvent evaporation/sample reconstitution after the extraction.

Acknowledgements
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References
[1] S.S Saini, A. Kabir, A. L. J. Rao, A. K. Malik, K. G. Furton, A novel protocol to monitor trace levels of selected polycyclic aromatic hydrocarbons in environmental water using fabric phase sorptive extraction followed by high performance liquid chromatography-fluorescence detection. Separations 4 (2017), 22.
[2] N. Manousi, G. A. Zachariadis, Recent Advances in the Extraction of Polycyclic Aromatic Hydrocarbons from Environmental Samples. Molecules 25 (2020), 1–31.

Dispersive Liquid-Liquid Microextraction Based on the Solidification of the Floating Organic Droplet using a Menthol-Based Deep Natural Eutectic Solvent for the Extraction of Phthalic Acid Esters from Soft Drinks and Infusions

P-2

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Keywords: *Dispersive liquid−liquid microextraction based on the solidification of the floating organic drop, high-performance liquid chromatography, L-menthol, natural deep eutectic solvent, phthalic acid esters.*

Deep eutectic solvents (DESs) are nowadays in the spotlight of investigation of a wide number of disciplines. The main reason is clear: the fulfilment of many Green Chemistry principles when they are used [1]. In general, DESs have a low toxicity, can be highly biodegradable, and they are normally easy to prepare without further purification steps if a proper synthetic design is developed. In this sense, the search for more biodegradable and environmentally friendly DESs has led to the appearance of natural DESs (NADESs), formed from certain natural products [2]. DESs are playing an especial role as extraction solvents in liquid-phase microextraction techniques and, in particular, in its dispersive version (DLLME). However, DLLME based on the solidification of floating organic drop (DLLME-SFO), which emerged as an advantageous alternative making the procedure faster, simpler, and safer [3], has been hardly explored using DESs as extraction solvents. Because of their toxicity, their ubiquitous prevalence in the environment, their extended use as plasticisers in plastic industry and human exposure, the use of phthalic acid esters (PAEs) is currently regulated by the European Union or the US Environmental Protection Agency, among others, even stablishing specific migration limits for some of them from plastic materials intended to be in contact with food. Considering this fact, in this work, the application of a previously synthesized L-menthol-based NADES (L-menthol:acetic acid 1:1, molar ratio) [4] has been extended to other more complex matrices using for the first time a DLLME-SFO procedure for the extraction of nine PAEs (i.e., dipropyl phthalate, butyl benzyl phthalate, dibutyl phthalate, diisopentyl phthalate, di-n-pentyl phthalate, dicyclohexyl phthalate di(2-ethylhexyl) phthalate, diisononyl phthalate, and diisodecyl phthalate) from three soft drinks (green tea, tonic and lime and lemon drink) and three infusions (chamomile, pennyroyal mint and linden teas) contained in plastic bottles and cans, using dihexyl phthalate and di-n-octyl phthalate as internal standards.

High-performance liquid chromatography with UV detection was used for the determination of the selected analytes. Relative recovery values were between 71 and 125 %, with relative standard deviation values in the range 1-22 % for the six types of samples, while the limits of quantification of the method were in the range 3.5-33.3 µg/L for soft drinks and between 4.3 and 51.1 µg/L for infusions. Additionally, three samples from different brands of each matrix were analysed. DPP, DBP, DIPP, DEHP and DINP were found in some of them, but only DPP, DBP and DEHP could be quantified at concentrations ≤ 49.7 ± 4.97 µg/L.

Acknowledgements

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References

[1] A. Shishov, A. Bulatov, M. Locatelli, S. Carradori, V. Andruch, Application of deep eutectic solvents in analytical chemistry. A review, Microchem. J. 135 (2017) 33-38.

[2] I. Pacheco-Fernández, R. González-Martín, F.A. e Silva, M.G. Freire, V. Pino, Insights into coacervative and dispersive liquid-phase microextraction strategies with hydrophilic media—A review, Anal. Chim. Acta. 1143 (2021) 225-249.

[3] F.R. Mansour, N.D. Danielson, Solidification of floating organic droplet in dispersive liquid-liquid microextraction as a green analytical tool, Talanta.170 (2017) 22-35.

[4] C. Ortega-Zamora, J. González-Sálamo, C. Hernández-Sánchez, J. Hernandez-Borges, Menthol-based deep eutectic solvent dispersive liquid-liquid microextraction: A simple and quick approach for the analysis of phthalic acid esters from water and beverage samples, ACS Sustainable Chem. Eng. 8 (2020) 8783-8794.

Determination of Drugs of Abuse in Saliva Samples via Dual-Template Molecularly Imprinted Paper and Direct Infusion Mass Spectrometry

P-3

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Keywords: *Cocaine, Direct infusion mass spectrometry, Methamphetamine, Molecularly imprinted polymer, Paper-based sorptive phase*

The field of sample pretreatment is of high importance in order to suppress the so-called matrix effect derived from complex matrices, however, it is also the most time-consuming step of the analytical procedure. For this reason, this discipline has been deeply investigated in the last decades in order to create new strategies that allow rapid and reliable procedures. In this context, paper has emerged as a very promising material due to its multiple advantages, such as the possibility of retaining compounds on its cellulose fibers or the spontaneous fluidic transport based on its own capillary action. In addition, it is a highly available and cost-effective material that can be easily coupled to various instrumental devices thanks to its flexibility and portability; and also be chemically modified to broaden its application scope [1].

On the other hand, although the selectivity of the method is improved, chromatographic separation significantly increases the analysis time. Even so it is usually mandatory prior to mass spectrometry to avoid matrix effect problems. However, this step can be avoided by previously isolating the analytes from the interferences via the use of sorbents.

The design of a new sorbent is a tedious process in which selectivity must be deeply considered. In the last decades, the molecularly imprinting technology has been consolidated and numerous approaches concerning molecularly imprinted polymers (MIPs) have been published [2, 3]. These materials possess artificially generated recognition sites towards a control molecule or a structural-related analogue, thus being able to isolate a certain compound while getting rid of the interferences.

In this context, a dual-template molecularly imprinted paper has been developed for the determination of drugs of abuse in saliva samples by direct infusion mass spectrometry. The MIP paper was obtained by dip-coating the paper with a polymeric solution (nylon-6 in formic acid) containing the templates, i.e., cocaine and methamphetamine. When the solvent evaporates, the polymer chains rearrange surrounding the templates, leaving the empty cavities once the MIP is washed. The as-synthesized MIP paper showed a better performance compared to the non-imprinted polymer and exhibited better affinity towards the analytes than for 6-acetylmorphine. Also, since the extraction is performed in an Eppendorf tube, multiple samples can be extracted simultaneously, thus increasing the sample throughput.

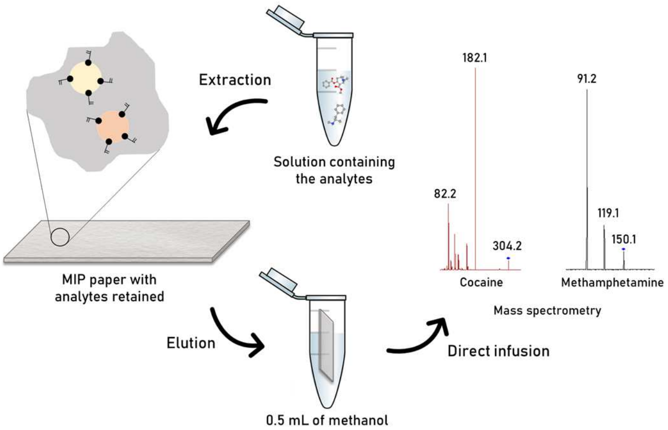

Figure 1. Extraction of cocaine and methamphetamine from saliva samples employing a molecularly imprinted paper and subsequent determination via direct infusion mass spectrometry.

Acknowledgements
Financial support from the Spanish Ministry of Economy and Competitiveness (CTQ2017-83175R) is gratefully acknowledged.

References

[1] E.W. Nery, L.T. Kubota, Sensing Approaches on Paper-Based Devices: A Review, Anal. Bioanal. Chem. 405 (2013) 7573-7595.

[2] M.C. Díaz-Liñán, A.I. López-Lorente, S. Cárdenas, R. Lucena, Molecularly Imprinted Paper-Based Analytical Device Obtained by a Polymerization-Free Synthesis, Sens. Actuators B Chem. 287 (2019) 138-146.

[3] P. Kadhirvel, A. Combès, L. Bordron, V. Pichon, Development and Application of Water-Compatible Molecularly Imprinted Polymers for the Selective Extraction of Carbamazepine from Environmental Waters, Anal. Bioanal. Chem. 411 (2019) 1525-1536.

Magnetic Paper Sorptive Phase for the Extraction of Parabens and Triclosan from Swimming Pool Waters

P-4

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Keywords: *Environmental sampling, magnetic membrane, microextraction, nylon-6, on-site extraction.*

The analysis of environmental waters is challenging due to the high volume of the systems (e.g., lake, river, sea) and the complexity of the sample matrix, where the analytes are at low concentration levels [1]. For that reason, the design of new sampling devices that integrate the preconcentration of target analytes is important. Furthermore, this isolation prevents the analytes degradation until sample processing. Those devices are mainly supported in microextraction techniques, solid-phase microextraction being the most used technique [2].

In this research work, a new magnetic sorbent was synthesized to improve the mass transference in a previously reported stir membrane sampling device [3]. Magnetic paper sorptive phase (MPSP) was synthetized by dip-coating method, and combines synergically the properties of nylon-6, magnetic nanoparticles, and paper as support. Magnetic nanoparticles promote the attachment to the extraction device, which is easy to employ and portable. The potential of the new material was evaluated in the determination of parabens and triclosan in swimming pool samples. Finally, to enhance the selectivity of the determination, mass spectrometry was used as instrumental technique. The limits of detection of the proposed method were in the range of 0.07 µg/L (butylparaben) to 0.1 µg/L (methylparaben and propylparaben). The precision at 5 µg/L in terms of relative standard deviation was always better than 8 %. And the accuracy of the proposed method was evaluated by spiking of the negative samples, and the relative recoveries were in the range of 88-98 %.

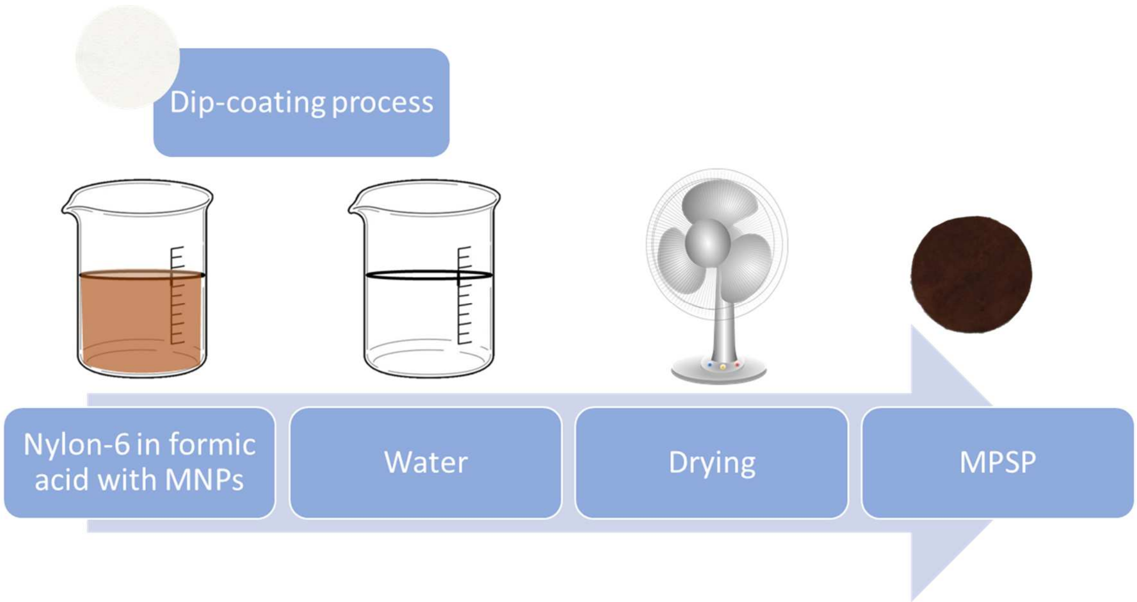

Figure 1. Synthesis process of magnetic paper sorptive phase.

Acknowledgements

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References

[1] D. Pérez-Bendito, S. Rubio, Chapter 3 Fundamentals of environmental sampling, in: Compr. Anal. Chem., Elsevier, 1999: pp. 59–117.

[2] H. Piri-Moghadam, F. Ahmadi, A critical review of solid phase microextraction for analysis of water samples, TrAC Trends Anal. Chem. 85 (2016) 133–143.

[3] F.A. Casado-Carmona, M. del C. Alcudia-León, R. Lucena, S. Cárdenas, Portable stir membrane device for on-site environmental sampling and extraction, J. Chromatogr. A. 1606 (2019) 360359.

High Throughput Determination of Three Drugs of Abuse by Direct Infusion Mass Spectrometry Using Nylon-6 Coated Wooden Toothpicks

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Keywords: *Drugs of abuse, high throughput analysis, mass spectrometry, saliva, wooden toothpicks.*

The use of widely available, affordable, and environmentally friendly sorptive phases is recommended in the microextraction context. There are plenty of natural materials that fulfill those requirements, including paper, cotton, cork, and wood, among others [1]. Wood is a natural biopolymer formed by cellulose, hemicellulose, and lignin that confers excellent properties (e.g., rigidity, porosity). The most wooden-based format that has been used in microextraction is wooden toothpick (WT) [2,3], but also wooden sticks have been used [4]. The multiple -OH groups available on the surface allow its coating with different polymers (and nanoparticles) by the dip-coating technique, boosting and introducing new interactions with the analytes. Most applications of WTs are related to their coupling to ambient pressure electrospray mass spectrometry in the so-called wooden-tip ionization electrospray mass spectrometry (WT-ESI-MS) technique. However, WTs can also be coupled to direct infusion mass spectrometry (DI-MS).

In this work, we present the use of nylon-6 coated wooden toothpicks (N6-WTs) for the determination of three different drugs of abuse, namely methadone (MTD), cocaine (CO), and methamphetamine (MTA) in saliva samples by DI-MS. N6-WTs were characterized by attenuated total reflection infrared spectroscopy and scanning electron microscopy (SEM) to confirm the presence of the polyamide (Figure 1).

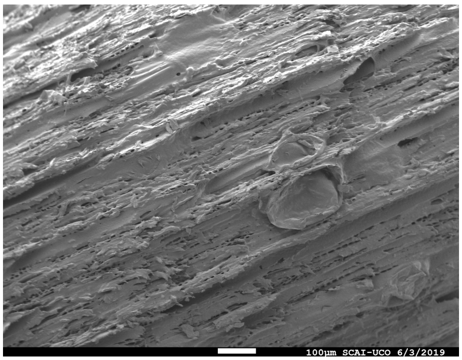

Figure 1. SEM illustration of the surface of a N6-WT.

The extraction process is carried out in different HPLC vials, allowing the extraction of multiple samples at the same time, and providing a high sample throughput of up to 22 samples per hour. The variables that significantly affect the extraction process (pH, extraction time, sample dilution, and number of dips) were optimized. Working under the optimum experimental conditions, the method provided limits of detection of 1.5 µg L^{-1} for all the analytes, allowing the corroboration of the existence of the drugs in forensic studies [5]. The dynamic range ($R^2 > 0.9849$) covered from 5 to 250 µg L^{-1} for MTD and CO, and up to 100 µg L^{-1} for MTA. The precision values, calculated as relative standard deviation (RSD) were in the range of 9.1 - 18.2%, and the accuracy, expressed as relative recovery, spanned from 86 to 103%.

Acknowledgements

Financial support from the Spanish Ministry of Economy and Competitiveness (CTQ2017-83175R) is gratefully acknowledged. J. Millán Santiago expresses his gratitude to the University of Córdoba for the grant "UCO. Becas Semillero de Investigación".

References

[1] G. Mafra, M.T. García-Valverde, J. Millán-Santiago, E. Carasek, R. Lucena, S. Cárdenas, Returning to nature for the design of sorptive phases in solid-phase microextraction, Separations 7 (2020) 1–22.

[2] B. Hu, P.K. So, H. Chen, Z.P. Yao, Electrospray ionization using wooden tips, Anal. Chem. 83 (2011) 8201–8207.

[3] T. Ng, P. So, B. Hu, Z. Yao, Rapid detection and quantitation of drugs-of-abuse by wooden-tip electrospray ionization mass spectrometry, J. Food Drug Anal. 27 (2019) 428–438.

[4] H. Karimiyan, M.R. Hadjmohammadi, K.L. Kunjali, M.M. Moein, J. Dutta, M. Abdel-Rehim, Graphene oxide/polyethylene glycol-stick for thin film microextraction of β-blockers from human oral fluid by liquid chromatography-tandem mass spectrometry, Molecules. 24 (2019) 1–12.

[5] H. Schulze, M. Schumacher, R. Urmeew, J. Alvarez, I.M. Bernhoft, H.G. de Gier, M. Hagenzieker, S. Houwing, A. Knoche, M. Pilgerstorfer, Driving Under the Influence of Drugs, Alcohol and Medicines in Europe—findings from the DRUID project, (2012) 1–58.

Combining Nanotechnology and Ultrasound: I*n Situ* Synthesis of Magnetic Nanocomposite for Mercury Preconcentration

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Keywords: *magnetite, magnetic nanocomposites, mercury analysis, preconcentration*

Mercury is included in the priority list pollutants, thus highly sensitive and selective methods are necessary for its determination, especially in drinking waters [1,2]. Lately, nanomaterial-based strategies have proved benefits in sensing and enrichment of pollutants [1]. In this work, ultrasound energy has been combined with nanotechnology allowing integration of main steps: *i.e.* synthesis of magnetite NPs and Hg(II) enrichment. An *in situ* ultrasound-assisted co-precipitation method was applied to prepare a magnetic nanocomposite for Hg(II) preconcentration in waters based on previous studies of the research group [3]. The novelty of this work lies on the combination of magnetite with noble metals for Hg(II) retention. Noble metals such as Ag(I), Au(III) and Pd(II) were added to the medium of synthesis allowing Hg(II) trapping. Then, easy magnetic separation of the Hg enriched-NPs from the aqueous phase was performed avoiding filtration or centrifugation steps. No elution was required either. Hg analysis was directly performed on 50 µL of the enriched magnetite nanocomposite in a direct mercury analyser (DMA) [4]. Among the noble metals attempted, best performance was provided by Pd. For 5 µg/L of Hg(II), a Hg/Pd ratio between 1:5 and 1:100 showed the highest increase in sensitivity. Characterization of nanocomposite was performed by transmission electron microscopy (TEM), high-resolution transmission electron microscopy coupled to energy dispersive X-ray spectrometry (HR-TEM-EDS) and total reflection X-ray fluorescence spectrometry (TXRF). The particle size was in the range 7-10 nm. The limit of detection obtained was 3.2 ng/L of Hg(II). The preconcentration factor achieved was 100 and the repeatability expressed as relative standard deviation (RSD, %) was 7 %. Trueness was evaluated using CRMs (water samples) containing different concentrations of Hg(II), namely, QC-1014, QC-1129 and QC-1205. Studies performed on real water samples yielded Hg recoveries in the range of 88-115 %. No satisfactory recoveries were found for wastewater samples due to the effect of organic matter on the direct synthesis of NPs in the water samples. The method is fast and efficient, allowing extraction and preconcentration of Hg in drinking water at ultratrace level.

Acknowledgements

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References

[1] J. Huber, K. Leopold, Nanomaterial-based strategies for enhanced mercury trace analysis in environmental and drinking waters, TrAC Trends Anal. Chem., 80 (2016) 280-292.
[2] K. Leopold, M. Foulkes, P. J. Worfsfold, Preconcentration techniques for the determination of mercury species in natural waters, TrAC Trends Anal. Chem. 28 (2009) 426-435.
[3] V. Romero, I. Costas-Mora, I. Lavilla, C. Bendicho, In situ ultrasound-assisted synthesis of Fe3O4 nanoparticles with simultaneous ion co-precipitation for multielemental analysis of natural waters by total reflection X-ray fluorescence spectrometry, J. Anal. At. Spectrom. 28 (2013) 923-933.
[4] I. de la Calle, J. Páez-Cabaleiro, I. Lavilla, C. Bendicho, One-pot synthesis of a magnetic nanocomposite based on ultrasound-assisted co-precipitation for enrichment of Hg(II) prior to detection by a direct mercury analyzer, Talanta 199 (2019) 449-456.

Development of Magnetic Nano-MIPs for the Selective Extraction of Proteins

P-7

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Keywords: *gold coating, core-shell particles, magnetic nanoparticles, molecularly imprinted polymers, silica polymer.*

The main objective of this project was the synthesis of core-shell magnetic nano-MIPs for the selective determination of ovalbumin (Figure 1). For this purpose, magnetic cores were prepared by a co-precipitation method and subsequently functionalized with a gold coating. Therefore, the gold-coated magnetic nanoparticles (Au-coated MNPs) demonstrated the ability to interact with the protein through the cysteine residues, allowing the union and orientation of this on the nanoparticles. Next, a silica polymeric layer was formed around it and, by removing the ovalbumin, selective cavities were created.

Polymerizations using both tetraethoxysilane (TEOS) and (3-mercaptopropyl)trimethoxysilane (MPTMS) as main monomer have been carried out. The combination of them with others functional monomers, including (3-aminopropyl)triethoxysilane (APTES) and phenyltriethoxysilane (PTES) were also tested and evaluated. In addition, the pre-attachment of MPTMS to the gold surface prior to the immobilization of the ovalbumin and the polymerization reaction has been proposed as a synthesis route to achieve a better and more homogeneous coating of nanoparticles with silica. Finally, the corresponding NIPs were prepared and characterized in terms of color/appearance, magnetism and aggregation. Clear macroscopic and microscopic differences were found between MIPs and NIPs, which demonstrated the participation of ovalbumin in polymerization. Finally, an ovalbumin rebinding study was carried out.

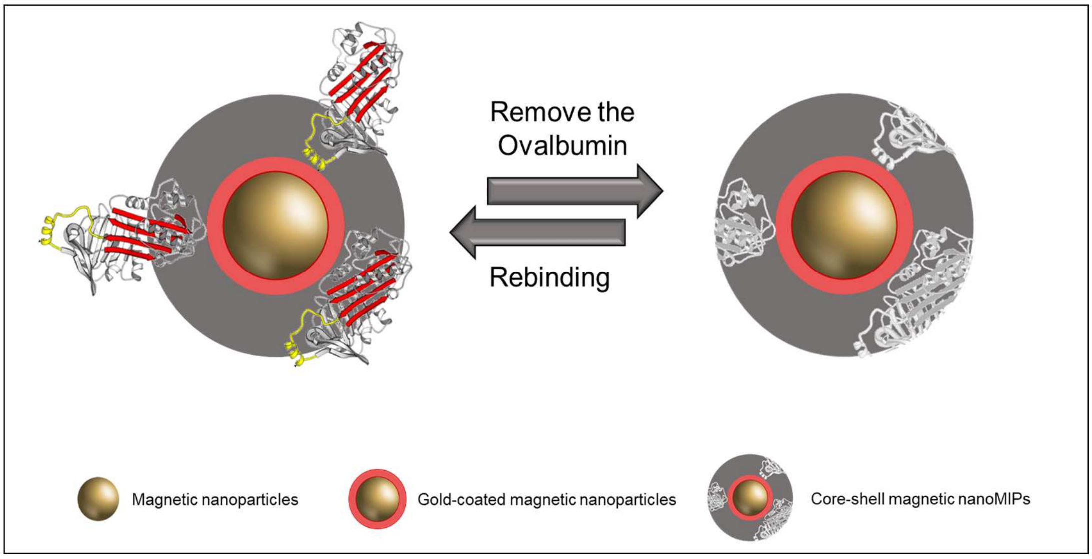

Figure 1. Developed core-shell magnetic nanoMIPs for the selective extraction of ovalbumin.

Preparation, Characterization and Application of C18 Thermally Immobilized onto Zirconized Silica as Sorbent for Solid-Phase Extraction

P-8

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Keywords: *endocrine disruptors, poly(methyloctadecylsiloxane), solid phase extraction, sorbent materials for SPE, zirconized silica-based materials*

In the study of complex aqueous environmental samples for the determination of organic contaminants (or pollutants), the step of eliminating interferents that may compromise the quality and reliability of the analytical results due to the matrix effect is especially important. Among the several techniques for solving problems related to the matrix effect in the extraction of complex samples, solid-phase extraction (SPE) is the most used technique due to its lower consumption of organic solvents, complying with the principles of Green Chemistry, and the possibility to enhancing the concentrations of analytes to posterior instrumental analysis by gas or liquid chromatography (GC or LC) [1,2]. Usually, SPE uses similar solid sorbent materials as in the stationary phases of LC, which have the function of extracting the analytes of interest from the aqueous matrices, being those based on silica modified with alkyl groups like C-8 or C-18 [3]. In this work, labmade sorbent materials were prepared modifying commercial silica structure (100 µm) with Zr alkoxide and poly(methyloctadecylsiloxane) (PMODS) (C-18), in order to evaluate the application of materials in the SPE extraction. For that, ultrapure water was fortified with standards classified as endocrine disruptors and emerging contaminants: bisphenol-A, phenanthrene and female hormones (estriol and 17α-ethinylestradiol) and the sample extracted by SPE, followed by the subsequent quantification by high performance liquid chromatography (HPLC) using diode array detection (DAD). The immobilization of the polymer under the zirconized silica was carried out using three different experimental conditions: 120 ºC for 16h, 160 ºC for 4 h, and 140 ºC for 6 h. The best results were obtained from the 120 ºC for 16 h condition, since the extraction efficiency were the highest: bisphenol-A and 17-α-ethynylestradiol with 85.4% and 102.4%, respectively, and for estriol and phenanthrene, 64.6% and 50,0%, respectively. The studies concerning about the breakthrough volume (off-line method, using 500 mg of sorbent *per* cartridge and aqueous standards of 25 mg/L of each compound) indicated that the sorbent obtained by the experimental condition of 120 ºC for 16 h retained all analytes until the passage of 250 mL of the sample, except for estriol (Figure 1). In addition, the physical-chemical characterization of the support indicated that metallization process provided a satisfactory incorporation of zirconium to the silica (54.2%, w/w), and that the PMODS was immobilized (physically sorbed and/or chemically attached) onto the silica-zirconized support. The application of Si-Zr(PMODS) sorbent in the extraction of four endocrine disruptors in water samples (labmade) evidenced that the material developed in this work presents potential to be used in the sample preparation of aqueous environmental samples using solid-phase extraction (SPE) followed by separation and quantification by HPLC-DAD.

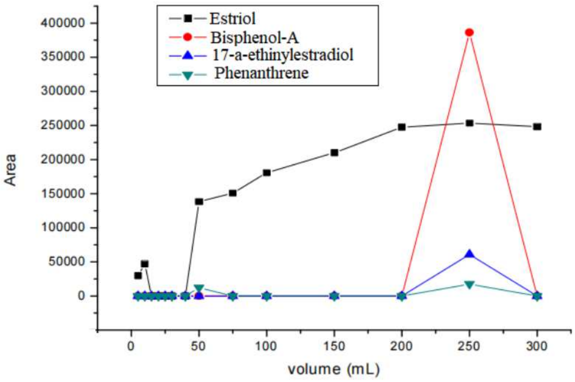

Figure 1. Breakthrough volume curves for the endocrine disruptors bisphenol-A, phenanthrene, estriol and 17α-ethinylestradiol, for the Si-Zr (PMODS) material prepared according to experimental condition of 120 ºC for 16 h.

Acknowledgements

The authors thank Prof. Carol H. Collins for her collaboration.

References

[1] I.C.S.F. Jardim, Extração em Fase Sólida: Fundamentos teóricos e novas estratégias para preparação de fases sólidas, Scientia Chrom. 2 (2010) 13-25.

[2] C.F Poole, New trends in solid-phase extraction, Trends Anal. Chem. 22 (2003) 362-373.

[3] A.M. Faria, C.H. Collins, I.C.S.F. Jardim, State-of-the-art in immobilized polymer stationary phases for high-performance liquid chromatography, J. Braz. Chem. Soc. 20 (2009) 1385-1398.

Thermal and Ultrasound Pretreatments for Enhancing Phenolic Recovery from Different Grape Extracts

P-9

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Keywords: *Grape, Natural Deep Eutectic Solvent, Polyphenols, Thermal Pretreatment, Ultrasound Pretreatment*

Biologically active compounds from plant material have been usually extracted by conventional solid-liquid extraction methods using toxic, volatile organic solvents. Nowadays, along with the growing recognition of the necessity to protect the environment, increased efforts are directed toward utilization of green solvents. Choline chloride based deep eutectic solvents have a high stabilizing ability for polyphenols, therefore they are used for sustainable and ecological friendly extraction of a broad range of compounds variety [1].

Present study is primarily focused on pretreatment techniques in order to facilitate the solubilization process and to enhance the phenolic recovery from grape, as a rich source of secondary metabolites, such as phenolic acids, flavanols, flavonols, anthocyanins and proanthocyanidins [2]. Total polyphenol content (TPC) determined by spectrophotometric method was an output parameter for choosing optimal pretreatment conditions. Heating (H) and ultrasounds (US) were used as a prior step to the conventional extraction (shaking maceration for 30 minutes), but with an emphasis to different conditions in order to expand previous investigations [3]. Namely, the thermal treatment was carried out at three points (40, 50 and 60°C). Impact of US pretreatment was contemplated at two frequencies (40 and 59kHz). In addition, we compared three different solvents regarding their extraction efficiency.

Obtained results revealed some interesting observations. Deep eutectic solvent choline chloride: citric acid (ChCit) absolutely outperformed conventional solvents (70% ethanol and water) regarding polyphenol extraction capacity. Thermal pretreatment evidently improved phenolic recovery in water extracts with no impact on extraction efficiency of two other solvents. Ultrasound pretreatment has no significant influence on TPC of extracts, however, US 59kHz for 10 minutes before conventional extraction with ChCit resulted in highest TPC. Overall, there is a need to perform a comprehensive study in order to better understand the underlying mechanisms of these remarks.

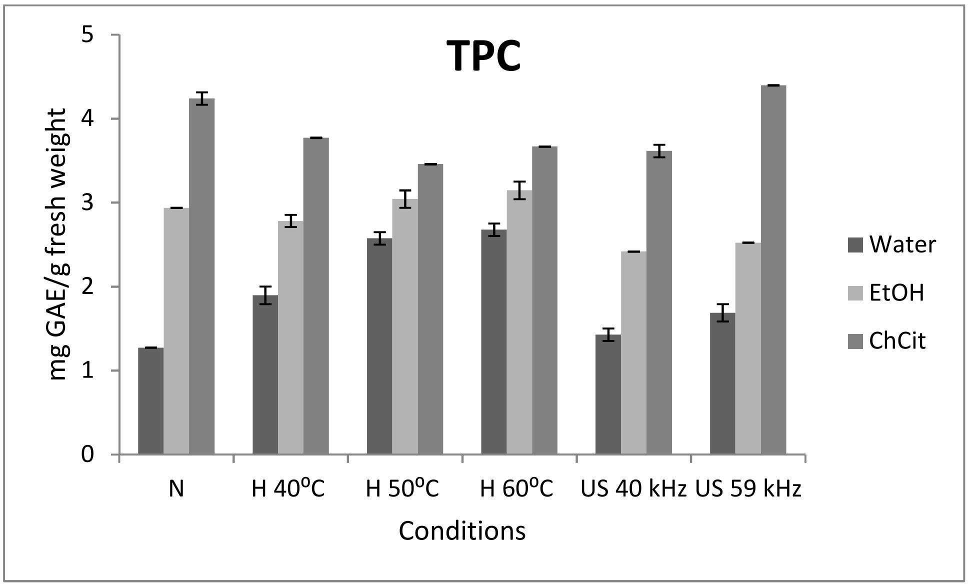

Figure 1. Total Polyphenol Content
*TPC- total phenolic content; GAE- gallic acid equivalents; N- no pretreatment; H- heating; US-ultrasound

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References

[1] K. Radošević, N. Ćurko, V. G. Srček, M.C. Bubalo, M. Tomašević, K.K. Ganić, I.R. Redovniković. Natural deep eutectic solvents as beneficial extractants for enhancement of plant extracts bioactivity. LWT, 73 (2016), 45-51.

[2] V. Georgiev, A. Ananga, V. Tsolova. Recent advances and uses of grape flavonoids as nutraceuticals. Nutrients, 6 (2014), 391-415.

[3] N. El Darra, N. Grimi, R.G. Maroun, N. Louka, E. Vorobiev. Pulsed electric field, ultrasound, and thermal pretreatments for better phenolic extraction during red fermentation. European Food Research and Technology, 236 (2013), 47-56.

μ-Separation of Petroleum Fractions Using a Metal-Organic Framework

P-10

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Keywords: *Advanced materials, mass spectrometry, petroleomics, sample preparation*

Petroleum is a complex mixture of saturated and aromatic hydrocarbons with heteroatom-containing compounds, i.e. resins and asphaltenes [1]. More than 30k molecular species have been identified in a single sample using ultra-high resolution mass spectrometry. A typical North Sea crude is medium-light and contains 70% saturates, 25% resins with approximately 5% resins and <1% asphaltenes [2]. Full molecular characterization is important for processing, recovery and environmental aspects. However, it is hindered by time-consuming and solvent heavy pre-fractionation methods. Reducing sample and solvent volumes are an important step towards greener sample preparation methods [3].

Metal-organic frameworks (MOFs) are porous coordination polymers formed via self-assembly. Their high surface area combined with the possibility of chemical functionalization of the internal pores make MOFs excellent candidates for advanced sample preparation and separation. The MOF HKUST-1 is constructed from copper paddlewheels connected by 1,3,5-benzenetricarboxylic acid linkers [4]. The framework contains two channels of different size, as well as two types of adsorptive sites; 1) π – π binding to the organic linker and 2) lone-pair electrostatic interactions to the free Cu^{2+} sites. This enables selective adsorption of aromatics and N,S,O-type compounds without binding of the saturates. By sequential application of extraction solvents, we demonstrate how HKUST-1 can be used for rapid microseparation of the saturated, aromatic and resin fractions of crude oil. Sub-microliter volumes of oil and less than 1 mL of solvent is used. This is in contrast to comparable methods, which often require multiple column chemistries and large sample and solvent volumes [5,6]. The method is thus highly suited for applications where only very limited amount of sample is available, e.g. microfluidic process studies (enhanced oil recovery, produced water management) [7]. Furthermore,

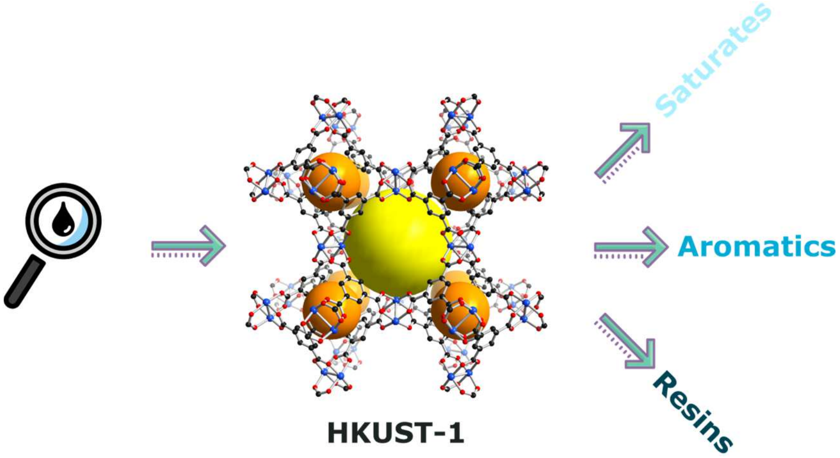

Figure 1. Simplified workflow and crystallographic representation of the different pores and adsorptive sites in HKUST-1

References
[1] R.P. Rodgers, A.G. Marshall, Petroleomics: Advanced Characterization of Petroleum-Derived Materials by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). Asphaltenes, Heavy Oils, and Petroleomics, New York, NY, 2007.
[2] J. Sundberg, K.L. Feilberg, Characterization of Heteroatom Distributions in the Polar Fraction of North Sea Oils Using High-Resolution Mass Spectrometry, J. Petroleum Sci. Eng. 184 (2020) 106563.
[3] M. Tobiszewski, A. Mechlińska, B. Zygmunt, J. Namieśnik, Green Analytical Chemistry in Sample Preparation for Determination of Trace Organic Pollutants. TrAC Trend. Anal. Chem. 28 (2009) 943–951.
[4] S.S. Chui, S.M.-F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. Williams, A Chemically Functionalizable Nanoporous Material [Cu3(TMA)2(H2O)3]n. Science 283 (1999) 1148–1150.
[5] W.J. Robson, P.A. Sutton, P. McCormack, N.P. Chilcott, S.J. Rowland, Class Type Separation of the Polar and Apolar Components of Petroleum. Anal. Chem. 89 (2017) 2919–2927.
[6] P.S. Ferreira, N.C.L. Madeira, G.S. Folli, W. Romão, P.R. Filgueiras, R.M. Kuster, Fractions from Light, Medium and Heavy Oils: Correlation between Chemical Profile and Stationary Phases. Fuel 274 (2020) 117866.
[7] V.A. Lifton, Microfluidics: An Enabling Screening Technology for Enhanced Oil Recovery (EOR). Lab Chip 16 (2016) 1777–1796.

Long-Term Evaluation of AAS Quality Control Data for Sample Preparation for Metal Analysis–Examples from Practice

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Keywords: *AAS, Environment Analysis, Metals, Sample Preparation*

Internal quality control is an essential feature of routine analysis that involves continuous critical evaluation of the used analytical methods and working routines, which serves to ensure that the uncertainty of results found during the validation of a procedure is maintained over long periods of time. The most important tool in quality control is the use of control charts and reference materials. The analyst runs control samples together with every series of prepared samples. Values are plotted in a control charts and they are compared to control and warning limits. This approach guarantees the accuracy and the stability of the results and protects against errors because you can immediately detect and remove such errors [1, 2]. Heavy metals have received a paramount attention to environmental chemists due to their toxic nature. They are usually present in trace amounts in the environment, but their toxicity is pronounced even in very low concentration. From the aspect of quality control and obtaining reliable results, one of the key factors is sample preparation [3, 4]. The sample preparation method varies according to the sample matrix (water, sediment or soil) and the analytical method used. However, most trace metal analysis procedures require the sample to be in liquid form, that usually require sample treatment or digestion depending on the complexity of the sample e.g. digestion by microwave method. Acid digestion is typically used to ensure the trace metal elements are completely dissolved [5-8]. In this study, analytical procedure for sample preparation was monitored by routine quality control out by certificate reference material for the period of five years. The obtained results from 5 years period are used for the preparation of X control charts, in order to confirm the laboratory performance for the metal analysis in according to Standard ISO/IEC 17025:2017. Based on the obtained results for analyzed metals, it can be concluded that the number of cases where the results were outside the warning limits was below 5 of total of 71 analyses. Examples of X control chart for Cu is given in Figure 1.

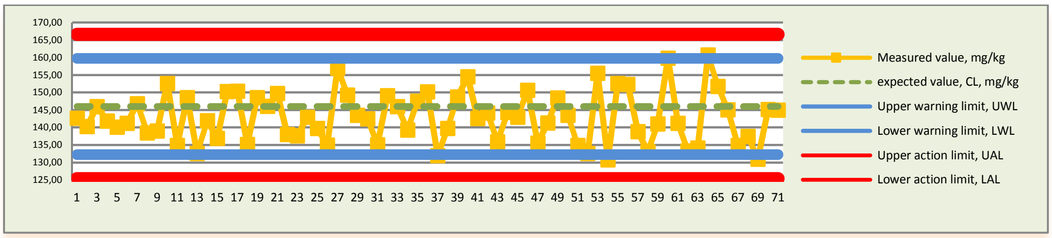

Figure 1. Example of X-chart for the analysis of copper in certificate reference material

In order to overcome problems with gained values in daily work, different approaches could be used (e.g controlling reagent quality, the method calibration, vessels and apparatus checking). The experience of the analyst is the most important for choosing appropriate remedial actions. In addition, the number of cases where the results were outside the warning limit was below 5 (with 71 last data points in X Chart) which indicated that the spread of analysis has not changed. Taking all these into consideration, the method for sample preparation of certificate reference material analysis in samples was under control and the quality of analysis did not change significantly over the five years period.

Acknowledgements
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References

[1] NORD TEST Report TR537. Handbook for calculation of measurment unceartainty in environmental laboratories. Bertil Magnusson,Teemu Naykki, Mikael Krysell. 2011.
[2] Directive 2009/90/EC of 31 July 2009 laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status. Official Journal of the European Union.
[3] S. Chowdhury, M.A. Jafar Mazumder, O. Al-Attas, T. Husain, Heavy metals in drinking water: Occurrences, implications, and future needs in developing countries. Sci. Total. Environ. 569 (2016) 476-488.
[4] M.S. Sankhla, M. Kumari, M. Nandan, R. Kumar, P. Agrawal, Heavy Metals Contamination in Water and their Hazardous Effect on Human Health-A Review. Int. J. Curr. Microbiol. App. Sci 5 (2016) 759-766.
[5] EPA 3015A – Microwave assisted acid digestion of aqueous samples and extracts, Revisia 1 February 2007.
[6] EPA 3051A – Microwave assisted acid digestion of sedimens, sludges, soils and oils, Revisia 1 February 2007.
[7] EPA7010 – Graphite furnace atomic absorption spectrophotometry, Revision 0 February 2007.
[8] EPA7000B – Flame atomic absorption spectrophotometry, Revision 2 February 2007.

Hollow Fiber Membrane-Protected Molecularly Imprinted Microspheres for Micro Solid-Phase Extraction and Clean-Up of Thiabendazole in Citrus Samples

P-12

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Keywords: *Hollow fiber membrane, Imprinted polymers, Micro solid-phase extraction, Thiabendazole*

In the present work, molecularly imprinted microspheres packed inside a polypropylene capillary has been prepared and further used for the hollow fiber membrane protected-molecularly imprinted micro solid-phase extraction (HFM-protected-MI-MSPE) of thiabendazole (TBZ) from citrus samples.

The presence of the hollow fiber avoids the direct contact between the MIP microspheres and the solid matrix allowing the selective extraction and clean-up in the same step without additional treatments such us centrifugation or filtration. After the optimization of the experimental conditions, TBZ recoveries were 5.1 and 6.1% for orange and lemon peel samples respectively, with relative standard deviations (RSDs) lower than 4%. The limits of detection were found to be 0.004 mg kg^{-1} and 0.009 mg kg^{-1} for orange and lemon samples, respectively, low enough for the determination of TBZ according to European Union legislation.

Figure 1. Vial containing the sample with the packed capillary to start the direct extraction.

An Integrated Sample Preparation/Sensing Approach for Iodide Determination Involving Polyvinylpyrrolidone-Protected Copper Nanoclusters

P-13

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Keywords: *Copper nanoclusters, Iodide, Luminescence, Microextraction, Optical sensing*

Currently, there is an increasing interest in the determination of anions such as iodide in environmental samples by implementing nanomaterials to accomplish suitable sensing approaches [1]. Notwithstanding this, several methodologies reported in the literature with this aim show limited sensitivity and selectivity [2,3], thus compromising the trueness and precision of obtained results when applicable. The development of straightforward approaches that can efficiently detect trace levels of iodide with increasing selectivity is therefore highly convenient. Bearing in mind the complexing ability of polyvinylpyrrolidone (PVP) toward I_2 and I_3^- [4], PVP-protected copper nanoclusters (PVP-CuNCs) were proposed as luminescent probes in a three-phase microseparation system for the selective and sensitive determination of iodide in environmental waters [5]. In particular, PVP-CuNCs were employed as extractant phases in single-drop microextraction (headspace mode) in combination with microvolume fluorospectrometry for the determination of the halide. The method involves *in situ* generation of molecular iodine, its further transfer to the headspace of the vial and trapping by an aqueous microdrop containing PVP-CuNCs. Several experimental parameters were evaluated for optimal response, including instrumental conditions and those variables related to the *in situ* formation and mass transfer of molecular iodine. Under optimal conditions, the method yielded limits of detection and quantification of 1.0 and 3.4 μg L^{-1}, respectively, and a repeatability, expressed as relative standard deviation, below 8% (N=7). Remarkably, an excellent enrichment factor above 1000 was achieved within 15 min. The proposed method was validated against a certified reference material and quantitative recoveries (97-108%) were achieved when the method was applied to the analysis of different water samples. Besides, PVP-CuNCs were characterized by transmission electron microscopy, time-resolved fluorescence, microvolume UV-vis spectrophotometry and fluorospectrometry in the absence and presence of molecular iodine for a better understanding of the sensing mechanism.

Acknowledgements

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References

[1] F. Pena-Pereira, A. García-Figueroa, I. Lavilla, C. Bendicho, Nanomaterials for the detection of halides and halogen oxyanions by colorimetric and luminescent techniques: A critical overview, TrAC, Trends Anal. Chem. 125 (2020) 115837.
[2] J. Zhang, X. Xu, C. Yang, F. Yang, X. Yang, Colorimetric iodide recognition and sensing by citrate-stabilized core/shell Cu@Au nanoparticles, Anal. Chem. 83 (2011) 3911-3917.
[3] K.V. Joshi, B.K. Joshi, U. Harikrishnan, M.B. Patel, S.K. Menon, Polyvinyl pyrrolidone modified ZnS nanoparticles as a highly selective and sensitive nanosensor for the iodide ion, Anal. Methods 5 (2013) 4973-4977.
[4] M.P. Arena, M.D. Porter, J.S. Fritz, Rapid, specific determination of iodine and iodide by combined solid-phase extraction/diffuse reflectance spectroscopy, Anal. Chem. 74 (2002) 185-190.
[5] F. Pena-Pereira, N. Capón, I. de la Calle, I. Lavilla, C. Bendicho, Fluorescent poly(vinylpyrrolidone)-supported copper nanoclusters in miniaturized analytical systems for iodine sensing, Sens. Actuat. B 299 (2019) 126979.

Surface Modified-Magnetic Nanoparticles by Molecular Imprinting For The Dispersive Solid-Phase Extraction Of Triazines From Environmental Waters

P-14

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Keywords: *Environmental waters, magnetic nanoparticles, molecular imprinting, solid-phase extraction, triazines*

Magnetic nanoparticles have been surface-modified by molecular imprinting and evaluated as selective sorbents for the extraction of triazines from environmental waters. The use of propazine as template allowed to synthesize a selective material able to simultaneously recognize and selective extract not only the template but also several other herbicides of the same family. A magnetic molecularly imprinted-based dispersive solid-phase extraction procedure was developed and fully optimized. Magnetic molecularly imprinted polymer particles can be easily collected and separated from liquid solvents and samples with the help of an external magnetic field, avoiding in that way any centrifugation or filtration steps, which represents a remarkable advantage over traditional procedures. Under optimum conditions, selective extraction of several triazines (cyanazine, simazine, atrazine, propazine, and terbutylazine) from environmental water samples was performed prior to final determination by high-performance liquid chromatography with diode-array detection. Recoveries for the studied triazines were within the range of 75.2–94.1%, with relative standard deviations lower than 11.3% (n=3). The limits of detection were within 0.16–0.51 µg/L, depending upon the triazine and the type of sample analyzed.

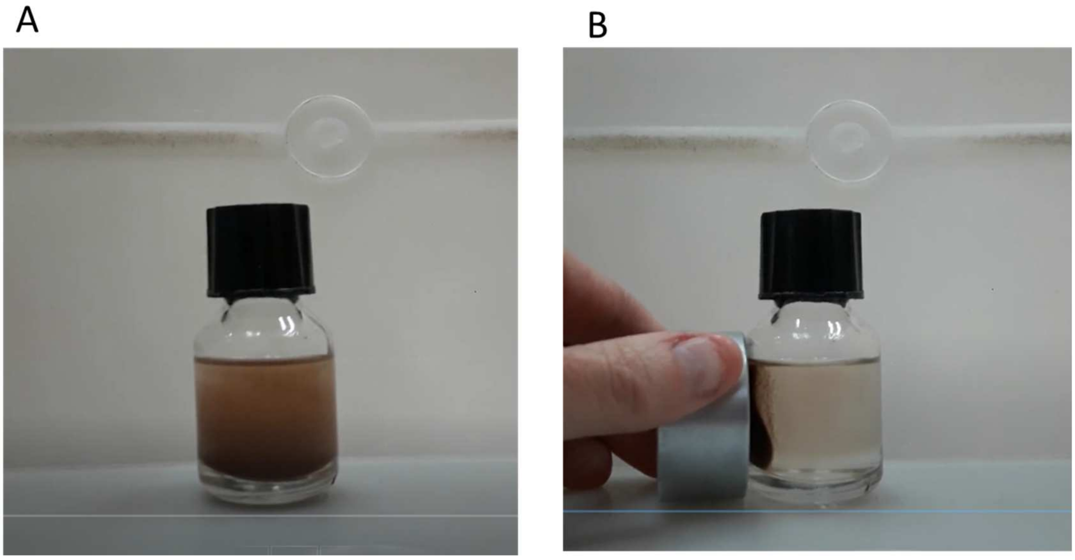

Figure 1. MMIPs suspended in the sample before (A) and after (B) applying a magnetic field

Multi-Cumulative Trapping HS-SPME to Enhance the Volatile Profile of Extra-Virgin Olive Oil

P-15

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Keywords: *Extra virgin olive oil, Headspace (HS), Multi-Cumulative Trapping, Solid-phase microextraction.*

Multiple-cumulative headspace-solid-phase microextraction (named MC-SPME) has been shown to be a very powerful technique to enhance the level of information on the volatile profile of foods. A fully automated multi-mode sample preparation system, containing a sorbent based focussing trap to retain and preconcentrate analytes, was used. The novel approach was investigated for the analysis of olive oil aroma profile using a pattern recognition approach. Different extraction parameters were investigated, e.g., extraction time, numbers of cumulative extraction, and, last but not least, the sample volume. Shorter cumulative extraction times proved to be more effective than a single longer extraction to provide more comprehensive profile of volatiles and semi-volatiles. Fundamental was the choice of a proper sample volume avoiding headspace saturation in order to maximize the exctraction of the semi-volatile compounds. This technique was successfully applied for the distinction of extra virgin olive oil, from the less expensive virgin olive oil and lampante oil [1,2]. Finally, the coupling of MC-SPME with GCxGC-MS provided a powerful platform for the detailed characterization of the extra-virgin olive oil aroma profile.

Acknowledgments
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References

[1] S. Mascrez, G. Purcaro, Enhancement of volatile profiling using multiple-cumulative trapping solid-phase microextraction. Consideration on sample volume, Anal. Chim. Acta 1122 (2020) 89-96.

[2] S. Mascrez, G. Purcaro, Exploring multiple-cumulative trapping solid-phase microextraction for olive oil aroma profiling, J. Sep. Sci 43 (2020) 1934-41.

Vacuum-assisted Headspace SPME: A Powerful Tool For Extra Virgin Olive Oil Profiling Enhancement

P-16

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Keywords: *Extra virgin olive oil, Headspace (HS), Solid-phase microextraction, Vacuum-assisted HS.*

Vacuum is a new experimental parameter to control and exploit during headspace microextraction (HS-SPME) method optimization and has been proved to be a powerful alternative to accelerate the extraction kinetics of analytes with a low affinity for the headspace [1]. The effect of this additional parameter was explored for the first time on a fatty matrix, namely olive oil. Extra virgin olive oil has a complex volatile aroma profile, which depends on several parameters (i.e., cultivar, geographical origin, fruit ripeness, processing practices, and storage). Past and current research efforts focus on unravelling the composition of this informative volatile fraction, so as to understand correlations with quality attributes. In the present work, the effects of extraction temperature and sampling time were investigated using traditional one variable at a time approach. The results showed a great improvement in the extraction of semi-volatile compounds using Vac-HS-SPME leading to an enhancement in the information gained by the olive oil aroma fingerprint [2]. The inherent complexity of the system requests further research to correlate thermodynamic conditions to the significant improvement in extraction conditions under non-equilibrium conditions.

Acknowledgments

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References

[1] E. Psillakis, Vacuum-assisted headspace solid-phase microextraction: A tutorial review, Anal. Chim. Acta, 986 (2017) 12-24.

[2] S. Mascrez, E. Psillakis, G. Purcaro, A multifaceted investigation on the effect of vacuum on the headspace solid-phase microextraction of extra-virgin olive oil, Anal. Chim. Acta, 1103 (2020) 106-114.

Improving the Performance of SPME Using Trap-Based Preconcentration with Enrichment

P-17

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Keywords: *Automation; Food quality; Food science; Sample Preparation; Trace Analysis*

Solid-phase microextraction (SPME) is a solventless sampling technique that is easily automated and avoids the inconveniences of solvent-based methods such as liquid/liquid extraction. However, using a standard GC injector for the fiber desorption requires careful optimisation, using a dedicated liner (<1 mm i.d) in conjunction with a high gas flow, in order to obtain optimum chromatography. In MS systems where carrier gas flow is limited, an injector split flow is therefore often used, but this reduces the quantity of analytes reaching the detector, and therefore the sensitivity of the technique.

Many of these disadvantages result from the desorption of the SPME fiber in combination with simultaneous injection of the analytes into the GC-MS system. By decoupling the desorption of the fiber from the injection into the GC-system these drawbacks can be overcome, resulting in higher sensitivity, while maintaining the other advantages offered by SPME. The addition of an electrically-cooled focusing trap after fiber desorption is what allows for the decoupling of desorption and injection. While high gas flows from SPME fiber to focusing trap allow for rapid desorption, the quick and efficient desorption of the focusing trap ensures that all the compounds reach the head of the analytical column simultaneously, leading to improved chromatography.

The focusing trap also allows a further increase in sensitivity by enabling the SPME fiber to return to the vial and extract for a second or third time, known as multi-step enrichment (MSE®). This enables a much more comprehensive profiling of samples. In this presentation, we demonstrate the effect of MSE improving the sensitivity achieved for volatile aroma and off-odour compounds in a tea sample, from 82 compounds identified for the regular SPME extraction to 113 compounds identified for a SPME-trap extraction and 229 compounds identified by SPME-trap with MSE.

Pressurized Hot Water Extraction Combined to SPME and GC×GC for Assessment of the Organic Fraction on Oil-bearing Source-rocks

P-18

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Keywords: *Biomarkers, Doehlert Design, Pressurized Hot Water Extraction, Solid-phase Microextraction, Two-dimensional Gas Chromatography.*

Traditionally, the methodology for analyzing organic biomarker compounds associated to oil and petroleum in rocks and sediments involves their extraction by Soxhlet type apparatus, followed by reconcentration of the organic fraction by solvent removal under nitrogen with subsequent fractionation of the extract by open-column liquid chromatography and analysis by GC-MS and/or –FID [1]. This procedure is time-consuming, costly and may not be reliable due to the excessive manipulation of the sample. The characterization and evaluation of the potential as an oil producer in a given basin is a challenge due to the high complexity and large number of constituents, which are often found in low concentrations [2,3]. Pressurized hot water extraction (PHWE) can be a valuable alternative to traditional methods for inspection of these samples, due to its efficiency, relative simplicity and to the compatibility of the aqueous extracts produced to be further proccessed by techniques such as SPME or SPE. Also, use of GC×GC instead of conventional GC can also result in further improvement of the procedure, allowing its simplification.

The optimization of a PHWE method for isolation of the organic fraction on oil-bearing rock samples was carried out using a multivariate strategy based on Doehlert Design. The sample used was a blend of previously characterized oil-bearing rocks. Three operational variables were optimized – hot water pressure, temperature and hot water flow. Experiments using combinations of seven level for extraction temperature, five levels of hot water extraction flow and three levels of hot water pressure were used. Since water vapor pressure is temperature-dependent, the pressure was indirectly optimized; the variable used on the experiments was a reduced pressure defined as $\mathbf{p_{red} = 100\ p_{abs} / p_v}$ (where $\mathbf{p_{abs}}$ is the absolute pressure of the system and $\mathbf{p_v}$ is the water vapor pressure at the temperature used). Tested levels $\mathbf{p_{red}}$ were 110 %, 150 % and 190 % relative to the water vapor pressure at the actual experimental temperature. In order to circumvent flow restriction limitations due to the dense packing of ground rock on the extraction cells (particles < 75 µm), samples were mixed with Ø ≈ 250 µm glass spheres (1 part sample : 5 pars spheres). After PHWE, 15 mL of the aqueous extract was re-extracted at 60 °C for 30 min by direct SPME using CAR/DVB/PDMS 50/30 fibers; SPME extracts were analyzed by GC×GC-MS.

Optimal conditions for PHWE were found to be T = 275 °C, p_{abs} = 110 bar (corresponding to p_{red} = 190 %) and extracting water flow of 2.5 mL/min. It was possible, using the optimized PHWE-SPME-GC×GC method, to obtain chromatographic fingerprints of aromatic hydrocarbons fraction using 35 mL of water for extraction and reduced sample amounts - *circa* 50× less (approx. 200 mg) than the standard method (10 g). It is also worth mentioning the absence of organic solvents in the method, while the conventional Soxhlet-SARA method can consume more than 500 mL per sample. It is believed that the amount of water can be reduced by checking the extraction kinetics, reducing the current water / sample ratio (160:1).

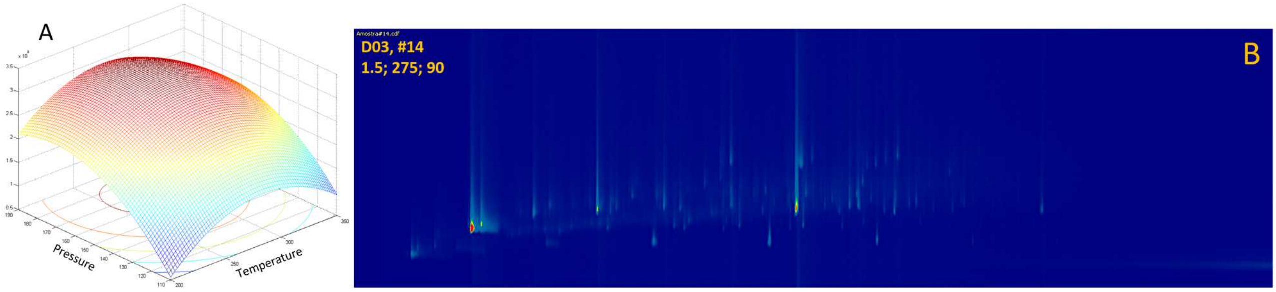

Figure 1. A) Doehlert Design response surface with fixed 2.5 mL/min flow rate. B) GC×GC chromatogram with extraction conditions of 275 °C, 90 bar and 1.5 mL/min.

Acknowledgements

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References

[1] P.S. Prata, G.L. Alexandrino, N.G.S. Mogollón, F. Augusto, Discriminating Brazilian crude oils using comprehensive two-dimensional gas chromatography-mass spectrometry and multiway principal component analysis, J. Chromatogr. A. 1472 (2016) 99–106.

[2] K.E. Peters, C.C. Walters, M. Moldowan., The Biomarker Guide. Biomarkers and isotopes in petroleum exploration and earth history, Cambridge, New York, 2005.

FPSE-HPLC-PDA Method for Rapid Determination of Solar UV Filters in Human Whole Blood, Plasma and Urine

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Keywords: *biological matrices, Fabric Phase Sorptive Extraction, HPLC-PDA, UV- filters, whole blood analysis*

Prolonged human exposure to solar UV radiation may result in acute and chronic health effects on the skin, eye and immune system (e.g. sunburns, skin cancers, cataracts, etc.). For this reason, there is a greater interest in minimizing solar UV radiation exposure and UV filters are incorporated in sunscreens formulations as well as in daily use cosmetics. UV filters, despite they are designed for external use, can be absorbed through the skin and different undesirable effects have been attributed to these compounds; thus, sensitive analytical methods to monitor biological levels of these compounds are in great demand.

The present poster describe an high performance liquid chromatography-photodiode array detection (HPLC-PDA) method for the simultaneous analysis of six benzophenone derivative UV filters including benzophenone (BZ); 5-Benzoyl-4-hydroxy-2-methoxybenzenesulfonic acid (BP-4); 4,4´-Dihydroxybenzophenone (4-DHB); 2,2´,4,4´-Tetrahydroxybenzophenone (BP-2); 2,4-dihydroxybenzophenone (BP-1); and 2,2´-Dihydroxy-4-methoxybenzophenone (DHMB) [1]. Chromatographic separation was conducted using a Spherisorb ODS 1 (C18) column in isocratic elution mode with a run time less than 25 minutes. The method was validated, in accordance with international guidelines, in the range from 0.1 to 10 μg/mL for all the UV filter compounds. Propyl 4- hydroxybenzoate was used as the internal standard (IS). The limit of quantification (LOQ) was 0.1 μg/mL, while limit of detection (LOD) was 0.03 μg/mL. The weighted-matrix matched standard calibration curves of six UV filters showed a good linearity up to a concentration of 10 μg/mL.

Prior to the HPLC-PDA analysis, these compounds were extracted from biological fluids (human whole blood, plasma and urine) through an innovative extraction technique, fabric phase sorptive extraction (FPSE). This new sample preparation technique, introduced in 2014, allows extraction of analytes through a direct contact between FPSE device and sample. The devices are constituted of natural or synthetic permeable and flexible substrate, chemically coated with a sol-gel organic-inorganic hybrid sorbent. This approach exhibits high recovery for the target analytes and allowed to reduce the amount of used organic solvents.

Additionally, fabric phase sorptive extraction membrane has been evaluated as a viable alternative to "*dried blood spot card* (DBS Card)" to collect droplets of whole blood spiked with the target UV filters and stored for a prolonged period after drying. The dried blood spots collected onto the FPSE membranes were found stable during the evaluated period up to 40 days with the analyte retention data comparable to the data obtained from whole blood droplets onto the FPSE membrane without prolonged storage.

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References

[1] M. Locatelli, K.G. Furton, A. Tartaglia, E. Sperandio, H.I. Ulusoy, A. Kabir, An FPSE-HPLC-PDA method for rapid determination of solar UV filters in human whole blood, plasma and urine, J. Chromatogr B 1118-1119 (2019) 40-50.

Development of a Miniaturized Solid-Phase Microextraction Methodology for the Analysis of Volatile and Semivolatile Compounds in Honey

P-20

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Keywords: *Honey, experimental design, miniaturized solid-phase microextraction, gas chromatography-mass spectrometry*

Honey is a product consumed worldwide and its use is justified by physicochemical, medicinal and nutritional characteristics. Properties of each honey are conditioned by their botanical and geographical origin. The biological value of honey is due to the presence of sugars, proteins, amino acids, enzymes, organic acids, vitamins, minerals, phenolic and volatile compounds [1, 2]. The aromatic profile of honey is important since it forms the organoleptic characteristics, identity and quality of honey. Aroma compounds are present in honey at low concentrations as complex mixtures of volatile components of different chemical families, and this composition depends on the floral origin of the nectar extracted by bees [3]. Solid-phase microextraction (SPME) is a very valuable extraction technique which offers the possibility of carrying out the extraction and pre-concentration of the target compounds in a single step.

The main goal of this work is the development of a miniaturized analytical methodology based on SPME followed by gas chromatography coupled to mass spectrometry (mini_SPME-GC-MS) for the determination of volatile and semi-volatile compounds in honey. This is the first time that 1.8 mL vials are proposed to carry out the SPME procedure employing a very low amount of honey.

Preliminary studies were performed employing a multifloral honey sample, to select some parameters such as extraction mode, water dilution and the possibility of miniaturizing the method, among others. Most critical parameters (i.e. type of fibre, extraction temperature, ionic strength and sample dilution) were optimized employing a fractional factorial design. Under the optimized experimental conditions, several extraction times between 5 and 60 minutes were studied. Method performance was evaluated in terms of linearity, precision (repeatability, reproducibility), and accuracy achieving satisfactory results. Once the method was validated, it was applied to a broad range of varieties of real honey samples, most of them from Galicia (NW, Spain), the only honey in Spain with Protected Geographical Identification [4].

Acknowledgements

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References

[1] V. Kaškonienė, P.R. Venskutonis. Floral markers in honey of various botanical and geographic origins: a review. Compr. Rev. Food Sci. F. 9 (2010) 620-634.
[2] M. Kortesniemi, S. Rosenvald, O. Laaksonen, A. Vanag, T. Ollikka, K. Vene, B. Yang. Sensory and chemical profiles of Finnish honeys of different botanical origins and consumer preferences. Food Chem. 246 (2018) 351-359.
[3] M.M.Rahman, M.N. Alam, N. Fatima, H.M. Shahjalal, S.H. Gan, M.I. Khalil. Chemical composition and biological properties of aromatic compounds in honey: An overview. J. of Food Biochem. 41(6) (2017) 12405.
[4] The Database of Origin & Registration (DOOR) from European Commission Website 2019. Available online: http://ec.europa.eu/agriculture/quality/door/list.html

Can Recycled Crumb Rubber Materials Spread Pollutants in Water? Evaluation of Water Leaches from Synthetic Turf Football Fields by HS-SPME-GC-MS/MS

P-21

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Keywords: *Hazardous organic compounds, recycled crumb rubber, solid-phase microextraction, synthetic turf football pitches, water leaches*

Nowadays, surfaces made of recycled crumb rubber from tires are employed as infill in synthetic turf football fields among other uses. These materials are usually outdoors, which means that meteorological conditions can affect them and spread part of its compounds in the environment. In addition, synthetic football fields during summer and on warm days require a periodic irrigation to maintain their properties. Therefore, chemicals like metals and organic chemicals (like polycyclic aromatic hydrocarbons or benzothiazole) in the rubber can be released with a potential negative impact on sewage water, groundwater and/or natural surface and even marine waters [1, 2]. Effect of rainwater and snowmelt on the mobility of pollutants in urban spaces was demonstrated in recent studies [3].

This study is focus on the assessment of the presence of 40 target compounds, including polycyclic aromatic hydrocarbons (PAHs), plasticizers, antioxidants and vulcanization agents in water adjacent to synthetic football pitches of diverse characteristics to estimate environmental risks. Diffusion of the target organic substances from the crumb rubber to the runoff water was evaluated analyzing water leachates collected from several football pitches. Also, the continuous leaching of these chemicals from the crumb rubber to the runoff water was simulated at lab-scale [4]. Analyses were carried out using headspace solid-phase microextraction followed by gas chromatography-tandem mass spectrometry (HS-SPME-GC-MS/MS) after a previous validation in terms of linearity, precision and accuracy. Optimum conditions of extraction such as type of fiber or extraction temperature was previously optimized [1, 5].

In view of the results, a relation between the water pollution and the chemical compositions of the crumb rubber football pitches exists. These results demonstrate the transfer of many of the target compounds, most of them considered as priority pollutants, into the runoff water, that can easily reach surface-waters or groundwater, representing a potential risk for the aquatic environment.

Acknowledgements

This research was supported by projects RETOS PID2019-104336RB-I00 (Ministry of Science and Innovation, Spain), UNST10-1E-491 (Infrastructure Program, Ministry of Science and Innovation, Spain), RED2018-102522-T (Ministry of Science, Innovation and Universities, Spain), to the Galician Competitive Research Groups IN607B 2019/13 and ED431 2020/06 and to the CRETUS Strategic Partnership ED431 2018/01 (Xunta de Galicia). This study is based upon work from COST Action CA16215 and 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). D. A. acknowledges European Cooperation in Science and Technology for his Short-Term Scientific Mission within COST Action CA16125.

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] M. Celeiro, D. Armada, T. Dagnac, J. de Boer, M. Llompart, Hazardous compounds in recreational and urban recycled surfaces made from crumb rubber. Compliance with current regulation and future perspectives, Sci. Total Environ. 755 (2020) 142566.

[3] A. Müller, H. Österlund, J. Marsalek, M. Viklander, The pollution conveyed by urban runoff: A review of sources. Sci. Total Environ. 709 (2020) 136125.

[4] 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, (2020) 128610.

[5] M. Llompart, L. Sanchez-Prado, J. P. Lamas, C. Garcia-Jares, E. Roca, T. Dagnac, Hazardous organic chemicals in rubber recycled tire playgrounds and pavers. Chemosphere, 90(2) (2013) 423-431.

Tropical Fruit Waste Valorisation Through Green and Sustainable Chemistry: Microwave Assisted Extraction

P-22

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Keywords: *Green and Sustainable Chemistry, Microwave Assisted Extraction, Bioactive Compounds, Waste Valorisation.*

The food supply chain (FSC) is a tradition industrial complex that generates, yearly, millions of tons of biomass that end up in the landfill, commonly considered as waste, or used in low-value applications, such as energy generation and animal feed [1]. A great part of the FSC residue is unavoidable, consisting mainly of non-edible fractions of food-related plants, such as seeds, peels, pulps, straws and kernels, which are obtained through plant-processing for food fabrication [2]. In Brazil, orange, mango and passionfruit are largely produced and their waste, as the majority of global food waste, is not properly used. These residues contain a vast number of bioactive compounds that could be re-inserted in the human diet (as in functional foods), used as health-promoting active ingredients (by the pharmaceutical industry) and in cosmetic applications. Examples of those high-value substances are hesperidin, hesperitin, naringenin and nobilitin from orange, hyperoside and mangiferin from mango and isoorientin, orientin and isovitexin from passionfruit, all having anti-inflamatory, antioxidant, antimicrobial activity, among other benefits. In this context, integration of the food waste in industrial processing for the extraction of bioactive compounds is a form of valorisation of the generated biomass, transforming it into valuable co-products [3, 4]. To reach this goal, the extraction technique needs to ensure enhanced yields, the use of greener resources and safer operation. For instance, the conventional organic solvent-based solid-liquid extraction using high-pressures and high-temperatures could be replaced by efficient, sustainable and industrially scalable techniques such as the Microwave Assisted Extraction (MAE), with ethanol mixtures in water. This work aims to develop and optimize extraction methods that meet both Green and Sustainable Chemistry requirements, employing MAE technology to achieve this goal. To optimize the experiments, chemometric tools were applied to reach the "greenest levels" of selected variables (temperature, time, solvent composition and sample to solvent ratio). The analysis of the extracts was carried out with HPLC-PDA and UHPLC-PDA. The parameters that achieve higher extraction yield for each fruit residue sample can be seen in **Table 1**.

Table 1. Extraction yield of bioactive compounds from different tropical fruits

Fruit waste	Compound	Independent variables				Yield
		Temperature	**Time**	**Sample to Solvent ratio**	**Solvent composition**	
		°C	min	-	$EtOH/H_2O$%	mg g^{-1}
Mango	Mangiferin	55	10	0.2	82.5	0.26
	Hyperoside					0.24
Orange	Hesperidin	150	5	0.05	80	21.6
	Hesperitin					0.15
	Naringenin					0.17
	Nobiletin					0.28
Passiflora	Orientin	120	5	0.1	30	0.82
	Isoorietin					0.94
	Isovitexin					0.34

Herein a novel method development to extract bioactive compounds of tropical fruit waste in a green and sustainable chemistry manner is presented. MAE appears a reliable sample preparation technique for this purpose, showing promising results that can be taken into consideration for upscale extraction in industrial scales.

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References

[1] J. Gustavsson, C. Cederberg, U. Sonesson, Global Food Losses and Food Waste, 2000.

[2] F. Girotto, L. Alibardi, R. Cossu, Food waste generation and industrial uses:A review, Waste Manag 45 (2015) 32–41.

[3] R.A. Milescu, M.L. Segatto, A.M. Stahl, C.R. McElroy, T.J. Farmer, J.H. Clark, V.G. Zuin, Sustainable Single-Stage Solid–Liquid Extraction of Hesperidin and Rutin from Agro-Products Using Cyrene, ACS Sustainable Chem. Eng. 49 (2020) 18245–18257.

[4] K. Kümmerer, J.H. Clark, V.G. Zuin, Rethinking chemistry for a circular economy, Science 367 (2020) 369–370.

Optimization of Pressurized Liquid Extraction and Evaluation of Antioxidant, Anti-Inflammatory and Anti-Alzheimer Activities In Vitro of *Ammodaucus Leucotrichus*

P-23

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***Keywords:** Ammodaucus Leucotrichus, anti-Alzheimer, anti-Inflammatory, Antioxidant, Pressurized-liquid extraction.*

The extraction of high added value products is an issue of great interest and importance especially when considering new plants growing in arid and semi-arid zones and which have not been studied enough. According to this objective, a spontaneous endemic plant; *Ammodaucus leucotrichus* originating from Saharian and sub-Saharian countries of north and tropical Africa, was selected. It is used in traditional medicine to treat stomach diseases, allergy symptoms, diabetes and cardiac diseases[1] and also in foods as condiment or flavouring agent [2].

Pressurized liquid extraction (PLE) is one of the most widely used techniques in extracting bioactive compounds from natural sources; PLE, also known as accelerated solvent extraction (ASE), can use a wide range of solvents at high pressure and temperature above their boiling point. It is an environmentally friendly, quick and efficient technology[3]; with the advantage of using very small amounts of solvent , hence avoiding the concentration stage.

PLE has been used for the first time to extract phenolic compounds from *Ammodaucus leucotrichus*, two environmental friendly solvents, water and ethanol, at different temperatures (40, 110 and 180 ºC) for 20 min at 10 MPa were applied in order to optimize extraction yield and total phenolic compound (TPC). Moreover, antioxidant activity by free radical scavenging (DPPH), anti-neurodegenerative by anticholinesterase (AChE) and anti-inflammatory by inhibition of lipoxygenase (LOX) were evaluated in vitro.

The results showed that *Ammodaucus leucotrichus* had significant antioxidant, anti-Alzheimer and anti-inflammatory activities. The optimal conditions were achieved at 180 ºC using water, which was a better extracting solvent than ethanol .Extraction yield was positively influenced by temperature in a range of 15.55 to 44.45%. Furthermore, antioxidant activity, inhibition of acetyl cholinesterase and inhibition of lipoxygenase showed the same behavior with the following EC_{50} values: 85.51µg/ml, 55.60ug/mL,39.37 ug/mL for DPPH, AChE and LOX, respectively.

In conclusion, the new PLE procedure can be considered as a green and efficient method for extracting phenolics from *Ammodaucus leucotrichus*, to obtain extracts with promising antioxidant, anti-Alzheimer and anti-inflammatory activities for future pharmaceutical and food applications.

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References

[1] Sadaoui N, Bec N, Barragan-Montero V, et al. The essential oil of Algerian Ammodaucus leucotrichus Coss. & Dur. and its effect on the cholinesterase and monoamine oxidase activities. *Fitoterapia*. 130 (2018) 1-5.
[2] Ziani BEC, Rached W, Bachari K, et al. Detailed chemical composition and functional properties of Ammodaucus leucotrichus Cross. & Dur. and Moringa oleifera Lamarck. *J Funct Foods*. 53 (2019) 237-247.
[3] Herrero M, Castro-Puyana M, Mendiola JA, Ibañez E. Compressed fluids for the extraction of bioactive compounds. *TrAC - Trends Anal Chem*. 43 (2013) 67-83.

Fabric Phase Sorptive Extraction of Tocopherols from Nut Oils Prior to Their High Performance Liquid Chromatographic Determination

P-24

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Keywords: *FPSE, HPLC, nut oil, tocopherols,*

Tocopherols play a substantial role in human nutrition and the main homologues detected in food matrices with biological importance are α-, β-, γ-, and δ- tocopherol. Following the current trends in sample preparation towards the development and advancement of green, miniaturized, rapid, simple, sensitive and robust sample preparation protocols that could be applied in the extraction of bioactive compounds from complex food matrices, a fabric phase sorptive extraction (FPSE) prior to High Pressure Liquid chromatography with UV detection (HPLC-UV) methodology was developed for the efficient extraction and further determination of tocopherols in nut oils. The proposed protocol involves the selection of a C18 FPSE membrane and the optimization of the following extraction parameters: the size of the FPSE membrane, the loading solvent type and volume, the type and volume of the elution solvent, the desorption time, and the extraction time. The chromatographic separation was accomplished with a Kromasil C18 column (150mm x 4.6mm x 5μm, Macherey Nagel) and gradient mobile phase consisting of methanol and acetonitrile at a flow rate of 1 mL/min. The total analysis time was 15 min. The developed methodology has demonstrated to be suitable and efficient for future applications in complex food matrices.

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Workflow for Integrated Quality and Safety Control of Dietary Supplements: Presence of Contaminants

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Keywords: *Dietary Supplements, Food contaminants, Overweight control, Quality Control, Sample Preparation*

Dietary supplements are increasingly being consumed in developed countries for different purposes. The high incidence of obesity and overweight problems in these societies [1], combined with the rise of specific aesthetic canons, have made nutritional supplements, marketed as aids for weight control, to be increasingly consumed by general population. Among them, those produced from vegetable sources are particularly well accepted because they are perceived as *natural* and, consequently, *harmless products*. However, some of these dietary supplements have been involved in several food and medical alerts and incidents due to the presence of contaminants and/or adulterants in their formulations, as well as misleading or incorrect labelling [2]. In many cases, the medical consequences derived from the uncontrolled presence of undesirable or not declared compounds are worsened by the fact that the consumption of these dietary supplements is often not controlled by a healthcare professional. During the last decade, the possibility of acquiring these types of plant-based supplements from third countries (often from not clearly identified or unknown producers) through the open internet market has contributed to aggravate the problem.

Safety and quality control of dietary supplements manufactured in developed countries or subjected to regular importation processes is guaranteed by current legislations. In general, these routine analytical controls are considered laborious and expensive in terms of time and reagents consumption because they usually involve separate analytical determinations for the different classes of compounds to be controlled, e.g. plant bioactives, adulterants, pharmaceuticals and contaminants. Meanwhile, products received from third countries by alternative channels frequently escape these exhaustive analytical determinations.

The aim on this study was the setting-up of a workflow that allowed the efficient, integrated and simplified analytical control of the previously mentioned groups of organic compounds in plant-based dietary supplements with minimum sample manipulation and reagent consumption. This poster summarizes the analytical strategy followed to implement the analysis of contaminants in such workflow. Satisfactory results demonstrate the general validity of the proposed approach for the generic screening of micro-contaminants through application to plant-based dietary supplements of different nature and from different sources and allowed to identify plasticizers as the main toxicants present in the investigated samples.

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References

[1] OECD (2010), Obesity and the economics of prevention: Fit not fat, OECD Publishing, Paris, https://doi.org/10.1787/9789264084865-en. [Last access: January 2021].

[2] NIH (2019), Dietary supplements for weight loss. U.S. Department of Health and Human Services. https://ods.od.nih.gov/factsheets/WeightLoss-Consumer/ [Last access: January 2021].

[3] A. Mena-García, S. Rodríguez-Sánchez, A.I. Ruiz-Matute, M.L. Sanz. Exploitation of artichoke byproducts to obtain bioactive extracts enriched in inositols and caffeoylquinic acids by microwave assisted extraction, J. Chromatogr. A 1613 (2020) 460703.

Green Analytical Chemistry Principles in Anionic Surfactant Detection by Potentiometric Sensors

P-26

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Keywords: *Anionic surfactants, Green chemistry, Potentiometric sensors, Wastewater*

Standard methods for anionic surfactants (ASs) determination are based on formation of the ion-pair compounds between the ASs and cationic dye methylene blue (MB): for real samples it is a volumetric method with visual end-point detection [1(a)], while for low levels of ASs in water it is a spectrophotometry of methylene blue active substance (MBAS) [1(b)]. This method suffers from several serious drawbacks such as numerous matrix interferences, use of chloroform – toxic and carcinogenic organic solvent, they are time-consuming, tedious etc., but still most commonly used all over the world.

Among many other analytical techniques, potentiometric determination of ASs with AS ion-selective electrode as indicator has numerous advantages: they are highly selective, fast and easy to perform, inexpensive etc. [2]. In term of sample preparation for real samples only dissolution is required, while for wastewater it is even simpler: the determination is performed directly in the water sample. Because of all these features it can be considered as a truly green analytical method [3].

In this investigations liquid-membrane potentiometric sensor with hexadecyltrioctadecylammonium-tetraphenylborate ion-pair (HTA-TPB) as ionophore was used as the end-point detector in potentiometric titrations [4]. Titrations were performed on model solutions (**Figure 1**),

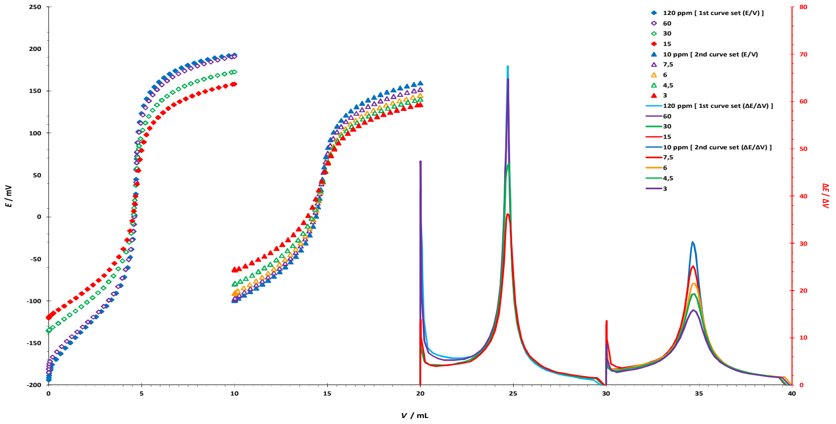

Figure 1. Titration curves and their corresponding first derivatives of NaDBS model solutions using HTA-TPB surfactant sensitive electrode and DMIC (c = 2 mM and 0,2 mM) as a titrant.

and on 6 samples: 3 real samples (products containing ASs) and 3 samples of industrial wastewaters. Results compared with results obtained by the standard methods **[1]** confirmed a high degree of agreement (**Table 1**).

Table 1. Results of potentiometric titrations of 3 real samples, and 3 wastewater samples with HTA-TPB sensor as the indicator. compared with the results obtained with standard methods.

	Real samples (%)		**Wastewater samples (mg/l)**	
Sample	**HTA-TPB**[1]	**ISO-2271**	**HTA-TPB**[2]	**ISO – 7875-1**
1	12,78	12,65	1,5	2,1
2	1,76	1,72	9,0	9,1
3	5,54	5,72	7,1	7,5

[1] Average of 3 determination; c_{DMIC} = 2 mM
[2] Average of 3 determination; c_{DMIC} = 0,2 mM

References

[1] (a) ISO 2271:1989 Surface active agents - Detergents - Determination of anionic-active matter by manual or mechanical direct two-phase titration procedure; **(b)** ISO 7875-1:1996. Water quality - Determination of surfactants - Part 1: Determination of anionic surfactants by measurement of the methylene blue index (MBAS).
[2] M. Jozanović, N. Sakač, M. Karnaš, M. Medvidović-Kosanović, Potentiometric Sensors for the Determination of Anionic Surfactants – A Review. Crit. Rev. Anal. Chem. (2019) 1–23.
[3] P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998, p.30.
[4] D. Madunić-Čačić, M. Sak-Bosnar, R. Matešić-Puač, A New Anionic Surfactant-Sensitive Potentiometric Sensor with a Highly Lipophilic Electroactive Material, Int. J. Electrochem. Sci. 6 (2011) 240-253.

No Sampling, the Best Sampling. Noninvasive and Micro-invasive Strategies for Cultural Heritage Studies

P-27

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Keywords: *Cultural Heritage, Non-invasive analysis, Micro-invasive analysis, X-Ray fluorescence, GC-MS*

Materiality of cultural heritage objects has become an analytical challenge. This is not only due to the well-known limited amount of sample that can be taken but also due to less visible drawbacks such as film and sample heterogeneity. The latter, laying on the basis that cultural heritage cannot be considered as a bidimensional entity but a tridimensional one,is usually composed by a complex overlapping of different micrometric layers [1,2]. In this work is presented the recent advances of the group in this regard for different applications in rock art, modern art and classical canvas paintings. Interestingly, the selected analytical strategies will strongly depend on the research question, going from a simple noninvasive analysis to a deep layered organic and inorganic characterization.

Regardless of this complexity, in agreement with the concept of “no sampling”, the first approach always consists of the screening of the object with noninvasive analytical techniques (Figure 1). In respect of this point, the group has developed a 3D X-Ray Fluorescence scanner (XRF) allowing for elemental characterization [3]. The XRF scanner allowed to get crucial information about inorganic information as well as abnormalities in the object as repainting, modifications done by the artist, and different paint layer overlapping. In addition, multispectral, UV, X-Ray transmission, among other techniques are also implemented to attain indirect information about chemical composition.

Nevertheless, the information collected by noninvasive approaches is not always suitable and sampling is needed. To this end, the sampling conditions must be extremely conservatives and, at the same time, representatives. Here, sample preparation of minute samples considering a layered or bulk analysis will clearly differ. On the one hand, for layered analysis (figure 1), cross-sections exposing all its constitutive strata are prepared followed by different μ-spectroscopic analyses [1,2]. On the other hand, as evidenced in figure 1, bulk analysis often dedicated to detailed organic composition determination implies the extraction, derivatization and sometimes preconcentration of these samples [4]. The work allowed to find molecular time markers employed for industrial paint relative dating in works of art. In this way, a series of advances and investigations are presented where the avoidance or minimization of sample size is required.

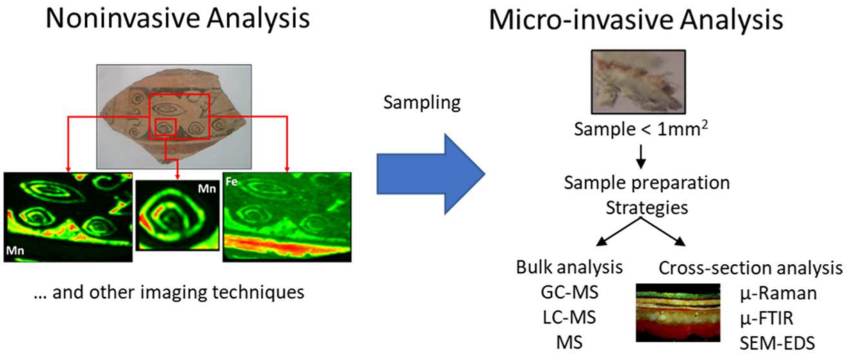

Figure 1. Scheme of a typical analytical workflow in cultural heritage.

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References

[1] M. Tascon, N. Mastrangelo, L. Gheco, M. Gastaldi, M. Quesada, F. Marte, Micro-spectroscopic analysis of pigments and carbonization layers on prehispanic rock art at the Oyola’s caves, Argentina, using a stratigraphic approach, Microchem. J. 129 (2016) 297–304.

[2] M. Tascon, N. Mastrangelo, D. Gallegos, F. Marte, Determination of materials and techniques involved in the mural paintings of San Miguel Church, Argentina, J. Raman Spectrosc. 48 (2017) 1356–1364.

[3] F. Taccetti, L. Castelli, C. Czelusniak, N. Gelli, A. Mazzinghi, L. Palla, C. Ruberto, C. Censori, A. Lo Giudice, A. Re, D. Zafiropulos, F. Arneodo, V. Conicella, A. Di Giovanni, R. Torres, F. Castella, N. Mastrangelo, D. Gallegos, M. Tascon, F. Marte, L. Giuntini, A multipurpose X-ray fluorescence scanner developed for in situ analysis, Rend. Lincei. 30 (2019) 307-322.

[4] F. Castellá, M. Pérez-Estebanez, J. Mazurek, P. Monkes, T. Learner, J.F. Niello, M. Tascon, F. Marte, A multi-analytical approach for the characterization of modern white paints used for Argentine concrete art paintings during 1940–1960, Talanta. 208 (2020) 120472.

Preconcentration of Selected Pesticides from Water Samples Using Coconut Shell Activated Carbon as Solid-Phase Extraction Adsorbent

P-28

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Keywords: *Coconut shell activated carbon, High performance liquid chromatography, Pesticides, Solid-phase extractiom, Water samples*

Pesticides released from agricultural practices are an important class of pollutants due to their widespread use, toxicity, persistance, polar nature and water solubility. Monitoring of the pesticides comprises a sample preparation procedure for extraction and preconcentration, and high performance instrumental techniques for quantification. Solid phase extraction (SPE) has been proved to be an effective sample pretreatment method due to high enrichment efficiency, low consumption of organic solvents, simplicity and easy operation. The choice of appropriate adsorbent is a crucial factor to obtain high recoveries and high enrichment factors in SPE procedure. In this study, the possibility of using activated carbon derived from coconut shell (CSAC) as the SPE packing material for the preconcentration of four varying polarity pesticides (Imidacloprid, Acetamiprid, Simazine, Linuron) from water samples prior to their determination by high performance liquid chromatography with diode array detector (HPLC-DAD) was investigated. The characteristics of the CSAC adsorbent were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) and Brunauer-Emmett-Teller (BET) method. The effects of the solution pH, eluent type, eluent volume and flow rate were investigated for optimization of the presented procedure. The obtained results indicated that the CSAC adsorbent had an excellent efficiency for the adsorption and recovery of pesticides in the pH range between 2.0 and 7.0. Dichloromethane (DCM) was chosen as the optimal elution solvent for simultaneous preconcentration and determination of the pesticides. Under optimized conditions, the proposed SPE method based on CSAC adsorbent exhibited good linearity, satisfactory precision (1.4 – 5.1%), high enrichment factor, good recovery and low LODs (0.025 – 0.039 $\mu g\ L^{-1}$).

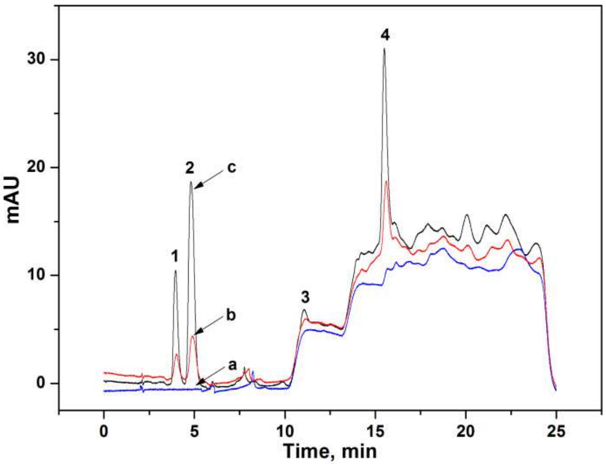

Figure 1. Chromatograms of extracted pesticides from a) unspiked tap water, b) and c) spiked tap water samples with 0.05 and 0.25 $\mu g\ L^{-1}$, respectively, after SPE-CSAC procedure under optimized conditions. Peak identification: 1) Imidacloprid, 2) Acetamiprid, 3) Simazine and 4) Linuron.

To test the applicability of the developed SPE-CSAC method, the analysis of four targeted pesticides in tap water samples collected in our laboratory was performed. Tap water samples were simultaneously spiked with each of the selected pesticides at two concentration levels (0.05 and 0.25 $\mu g\ L^{-1}$) and then analyzed by the developed method. Typical chromatograms obtained from unspiked tap water sample and tap water samples spiked with the selected pesticides at the concentrations of 0.05 and 0.25 $\mu g\ L^{-1}$ are shown in Fig. 1. The recoveries ranged from 58.2% to 105.3%, with low relative standard deviations.

Based on the obtained results, it can be concluded that the CSAC adsorbent could be efficiently used as a low cost alternative to commercially available SPE adsorbents and that the optimized SPE-CSAC method developed in the presented study has a large potential as an inexpensive and efficient sample preparation method, which could be widely used in the future for the determination of varying polarity pesticides at trace levels in environmental water samples.

Acknowledgements

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Evaluation of Method Performances for Polycyclic Aromatic Hydrocarbons Analysis in Sediment Using Gas Chromatography/Mass Spectrometry

P-29

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***Keywords:** GC-MS, polycyclic aromatic hydrocarbons, sediment, method validation*

Polycyclic aromatic hydrocarbons (PAHs) belong to a class of persistent organic pollutants and are ubiquitously present in the environment. As a consequence of high hydrophobicity, PAHs in aquatic environments tend to be rapidly brought down to the bottom sediment which represents the most important reservoir of PAHs in the aquatic environment. Due to their carcinogenic, mutagenic, teratogenic and genotoxic properties, PAHs are the subject of systematic monitoring in most countries worldwide [1]. The US Environmental Protection Agency (EPA) has included 16 PAHs on the list of priority substances, while naphthalene, anthracene and sum of PAHs are labeled as priority pollutants in accordance with the European Union Directive 2013/39/EC. A large group of PAHs have been in the focus of various studies regarding different methodologies, procedures and equipment for the determination of PAHs in environmental samples. Thus, this paper presents the results of evaluation of modified standard methods for PAHs analysis in sediment using gas chromatography/mass spectrometry (GC-MS).

PAHs were extracted from 3 g of sediment according to EPA3550b method [2] by ultrasound extraction technique with 15 ml of acetone/hexane mixture (1:1, v/v). Extraction procedure was repeated three times. Elemental sulphur was removed with copper powder technique [3]. Samples were fractionated over silica gel cleanup column using pentane (1st fraction), methylene chloride/pentane (2:3, v/v, 2nd fraction) and finally methylene chloride/methanol (9:1, v/v, 3rd fraction) [4], evaporated under nitrogen flow and analyzed using an Agilent 7890A Series GC with a 5975C MSD MS on a HP-5MS column (J&WScientific) using phenathrene-d10 as the internal standard [5,6]. Sediment samples weigh and recommended volume of extraction solvent/solvent mixture given in EPA methods was reduced considering required method performances as well as national guideline values for PAHs in sediment.

Method detection limit (MDL) and method quantitation limit (PQL) were determined by the measurement of 6 replicates of natural river sediment, and calculated according to the APHA-AWA-WEF method [7]. Estimated PQL were in range 9,2-11,1 µg/kg. Method precision and accuracy were determined by measuring six replicates in duplicate of fresh water sediment certified reference material (CRM) and spiked sediment samples. Recovery values for CRM and spiked sediment samples were in range 71-113% and for precision were ≤18% RSD which is in accordance with EPA 8000B method recommendation (70-130%). Control charts were further applied to monitor the characteristics of the applied analytical procedures such as accuracy and precision, in order to estimate measurement uncertainty which was generally about 40%.

The results of quality control program indicate that variation of method performance was not statistically significant in comparison with the parameters set during the validation experiments. Modified sample preparation protocol followed by GC-MS analysis can be used as a reliable method for the determination of PAHs in sediment samples which was also confirmed by Proficiency testing.

Acknowledgements

The authors acknowledge financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 451-03-68/2020-14/ 200125).

References

[1] S. Maletić, J. Beljin, S. Rončević, M. Grgić, B. Dalmacija, State of the art and future challenges for polycyclic aromatic hydrocarbons is sediments: sources, fate, bioavailability and remediation techniques, J. Hazard. Mater. 365 (2019) 467-182.

[2] EPA method 3550B (USEPA, 1996) Ultrasonic extraction, Revision 2.

[3] EPA method 3660B (USEPA, 1996) Sulfur cleanup, Revision 2.

[4] EPA method 3630C (USEPA, 1996) Silica gel cleanup, Revision 3.

[5] EPA method 8270C (USEPA, 1996) Semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS), Revision 3.

[6] S. Maletić, J. Beljin, D. Tamindžija, M. Grgić, J. Molnar Jazić, M. Kragulj Isakovski, S. Rončević, Bioremediation perspective of historically contaminated sediment with polycyclic aromatic hydrocarbons, Int. J. Sediment Res. doi.org/10.1016/j.ijsrc.2020.11.004.

[7] APHA, AWWA, WEF. Standard Methods for examination of water and wastewater. 22nd ed. Washington: American Public Health Association; 2012.

Utilization of DoE Approach to Optimize the Procedure of Modified Nucleosides and Deoxynucleosides Extraction for Targeted Metabolomic Analysis

P-30

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Keywords: *Design of Experiments, modified nucleosides, modified deoxynucleosides, solid-phase extraction*

Design of Experiments (DoE) is a statistical approach used to plan, optimize and conduct experiments [1]. It determines the relationships between factors and responses affecting a process. Moreover, variables are dependent on each other so that an effect of one factor is influenced by the settings of other parameters. Consequently, these interactions can be noticed by DoE methodology. Experimental plan is created to minimize experimental runs while attaining information-rich results. The goal of the presented study was optimization of sample preparation procedure allowing for simultaneous extraction of 12 selected modified nucleosides and deoxynucleosides with the use of solid phase extraction (SPE) technique. Modified nucleosides and deoxynucleosides are products of RNA and DNA catabolism. They are considered as potential markers of pathological disorders [2]. However, due to different molecular properties their concurrent extraction is challenging. In the present study, mixed-mode SPE sorbent, composed of phenylboronic acid and cation-exchange resins, was applied. The method was optimized with the use of DoE approach. Firstly, Fractional Factorial Design was applied. Examined variables were conditioning, washing and elution solvents compositions. Next step included Full Factorial Design with duration time of conditioning, sample loading and elution step as factors. Responses acquired in two experimental sets were peak areas of 12 analyzed modified nucleosides and deoxynucleosides. Levels of assessed factors were determined. Developed and optimized SPE procedure allowed for the extraction of modified nucleosides and deoxynucleosides with mean recovery of 76.0%.

Acknowledgements
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References

[1] J. Jacyna, M. Kordalewska, M.J. Markuszewski, Design of Experiments in metabolomics-related studies: An overview, J. Pharm. Biomed. Anal. 164 (2019) 598-606.
[2] M. Patejko, W. Struck-Lewicka, D. Siluk, M. Waszczuk-Jankowska, M. J. Markuszewski, Urinary nucleosides and deoxynucleosides, Adv. Clin. Chem. 83 (2018) 1-51.

Food Security in Wine Consumption

P-31

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***Keywords:** Sustainability, Food quality, QuEChERS, Pesticides*

Food security has become increasingly important, not only because of world population increase, but also as a result of global commercialization of products. In this sense, ensuring the correct handling and storage of foodstuff, as well as minimizing or eliminating food-borne illnesses are considered crucial issues [1].

The control of contaminants, such as pesticide residues is one of the main challenges in this area, due to their potential health risk [1]. In addition, different regulatory authorities, including the European Commission (EC) and the United States Food and Drug Administration (FDA), have established monitoring plans for these contaminants, as well as different directives that regulate this issue, in order to protect consumer safety and ensure products quality.

A clear example is the abusive use of pesticides as a measure against pests that attack different crops, especially in areas with an intensive agriculture. For these reasons, it is fundamental the development of analytical methodologies that allow monitoring these compounds, and guarantee safety in food consumption.

In this work, an analytical method has been applied for the determination of pesticide residues in red wine from different origins, using both gas and liquid chromatography coupled to mass spectrometry in combination with the QuEChERS method [2] as extraction procedure. The methodology was validated, following the SANTE/12682/2019 guide [3], obtaining good recovery values (with relative standard deviations lower than 20%) and a high sensitivity that allow strict monitoring of these compounds.

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References

[1] Y. Zhang, G. Li, D. Wu, X. Li, Y. Yu, P. Luo, J. Chen, C. Dai, Y. Wu, Recent advances in emerging nanomaterials based food sample pretreatment methods for food safety screening, TrAC-Trend. Anal. Chem. 121 (2019) 115669.

[2] M. Anastassiades, S.J. Lehotay, D. Štajnbaher, F.J. Schenck, Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and "Dispersive Solid-Phase Extraction" for the Determination of Pesticide Residues in Produce, J AOAC Int. 86 (2003) 412-31.

[3] Analytical quality control and method validation procedures for pesticide residues analysis in food and feed. Document Nº SANTE/12682/2019.

On-Line in-Syringe Ultrasound-Assisted Cloud Point-Dispersive Liquid–Liquid Microextraction for the Fluorescent Determination of Aluminum in Water and Milk Samples

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Keywords: *Aluminum; Cloud point-dispersive liquid–liquid microextraction; Ionic liquids; Syringe; Ultrasound energy*

In this work, a simple, fast and ecological method to determine aluminum in natural and mineral water, and milk samples was developed. Aluminum is a toxic element that can be found in packaging as well as in different containers. The World Health Organization has fixed limits for the presence of aluminum in drinking water and food [1]. Therefore, it is important to develop new reliable methods for its determination. This new procedure was performed by means of an in-syringe cloud point-dispersive liquid-liquid microextraction (Fig 1) using a mixture of an ionic liquid and a surfactant as extractant instead of organic solvents. 8-hydroxyquinoline was used as chelating agent to extract Al^{3+} with a subsequent online spectrofluorometric detection. Under the optimal conditions, the preconcentration factor was 200, and the recovery values were between 91.4-109.1% (n=3) with satisfactory % Relative Standard Deviation (%RSD) values, which indicate appropriate accuracy and precision. The limits of detection (LOD) were 1.7 and 5.5 µg L^{-1}, and the limits of quantification (LOQ) were 5.7 and 18.4 µg L^{-1} for water and milk samples, respectively. The obtained results demonstrated the applicability of the proposed method for the determination of aluminum in real water and milk samples. The main advantage of this research was that ultrasound energy was applied to improve the extraction and preconcentration steps, which was reflected in a reduction in the total analysis time. In addition, the method also complies with some principles of green chemistry [2], since it uses environmentally friendly solvents, a reduced volume of reagents, and generates low amounts of waste.

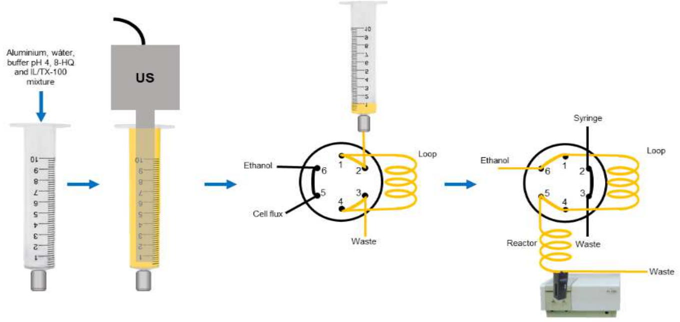

Figure 1: Procedure of the in syringe UA-CP-DLLME.

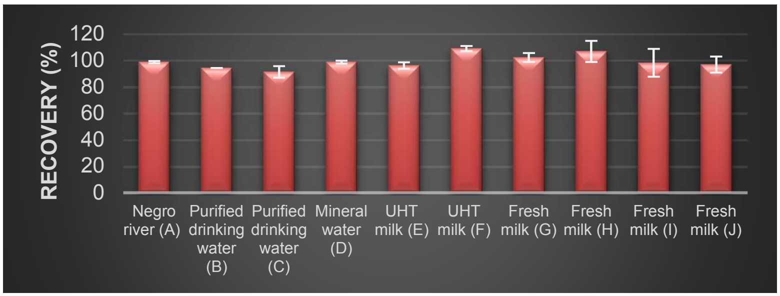

Figure 2: Recovery study for different water and milk samples analyzed by the developed method. One concentration level was tested (100 µg L^{-1}, n = 3).

References

[1] Joint Expert Committee on Food Additives. (2011). Evaluation of certain food additives and contaminants (Seventy-fourth report of JECFA) (pp. 7–18). WHO Technical Report Series.

[2] S. Armenta, F.A. Esteve-Turrillas, S. Garrigues, M. de la Guardia, Green analytical chemistry: the role of green extraction techniques. In Green Extraction Techniques: Principles, Advances and Applications, Elsevier, Amsterdam 2017, pp. 1-25.

A Molecularly Imprinted Polymer Based Electrochemical Sensor for the Determination of a Tyrosine Kinase Inhibitor Drug

P-33

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Keywords: *Axitinib, Electrochemistry, Drug analysis, Molecularly imprinted polymer*

The present study aims to develop a fast, selective, and sensitive method for the determination of Axitinib (AXI) at low concentrations in pharmaceutical dosage forms and human serum. For this purpose, a novel molecularly imprinted polymer (MIP)-based electrochemical sensor was developed through electropolymerization of o-phenylendiamine (o-PD) on GCE using cyclic voltammetry (CV). Additionally, differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) techniques were used to evaluate the performance of the newly developed MIP-based sensor. AXI, a second-generation targeted drug, is a highly selective and potent inhibitor of vascular endothelial growth factor receptor (VEGFR) tyrosines kinase 1, 2, and 3 [1]. Tyrosine kinases are used as therapeutic agents to treat different types of cancer. AXI is used for the treatment of renal cell carcinoma [2,3]. MIP-based electrochemical sensors are based mainly on a functional polymerization of monomers and the formation of cavities that can selectively recognize target molecules in any matrix [4]. They also have the advantageous properties of electrochemical techniques such as low-cost, high precision and simplicity [5]. In this work, a MIP film was formed through electropolymerization of the functional monomer o-PD on GCE using CV. In order to establish optimal experimental conditions; number of cycles for polymerization, monomer:template ratio, template removal treatment and incubation time for AXI were optimized. After optimization of experimental conditions, analytical performance of the MIP-based sensor was evaluated by the determination of different concentrations of AXI ranging from 1×10^{-13} M AXI to 1×10^{-12} M AXI were performed with MIP based sensor by DPV using 5 mM $[Fe(CN)_6]^{3-/4-}$ solution as redox marker. The regression equation for AXI was found as $\Delta Ip(\mu A) = 3.312\times10^{13}C\ (M)+36.036$ ($R^2=0.996$) for MIP based sensor. The limit of detection (LOD) value was calculated as 27 nM according to the equation of LOD=3s/m while the limit of quantification (LOQ) was found as 89 nM according to the equation of LOQ=10s/m. In order to demonstrate the applicability and validity of developed sensor, it was used for the determination of AXI in tablet dosage form and human serum sample. Additionally, The NIP based GCE was prepared with the same experimental process and conditions above without adding AXI during the electropolymerization step. NIP based electrochemical sensor was used for the control of the analytical performance of MIP based electrochemical sensor. The selectivity of the MIP/GCE sensor, which is the most critical validation parameter, was qualified by comparing the binding of AXI, erlotinib, dasatinib, nilotinib, and imatinib, which are AXI-like structured anticancer drugs.

References

[1] D.D. Hu-Lowe, H.Y. Zou, M.L. Grazzini, M.E. Hallin, G.R. Wickman, K. Amundson, J.H. Chen, D.A. Rewolinski, S. Yamazaki, E.Y. Wu, M.A. McTigue, B.W. Murray, R.S. Kania, P. O'Connor, D.R. Shalinsky, S.L. Bender, Nonclinical antiangiogenesis and antitumor activities of axitinib (AG-013736), an oral, potent, and selective inhibitor of vascular endothelial growth factor receptor tyrosine kinases 1, 2, 3, Clin. Cancer Res. 14 (2008) 7272–7283.

[2] M. Gross-Goupil, L. François, A. Quivy, A. Ravaud, Axitinib: A review of its safety and efficacy in the treatment of adults with advanced renal cell carcinoma, Clin. Med. Insights Oncol. 7 (2013) 269–277.

[3] K. Tzogani, V. Skibeli, I. Westgaard, M. Dalhus, H. Thoresen, K.B. Slot, P. Damkier, K. Hofland, J. Borregaard, J. Ersbøll, T. Salmonson, R. Pieters, R. Sylvester, G. Mickisch, J. Bergh, F. Pignatti, The European Medicines Agency Approval of Axitinib (Inlyta) for the Treatment of Advanced Renal Cell Carcinoma After Failure of Prior Treatment With Sunitinib or a Cytokine: Summary of the Scientific Assessment of the Committee for Medicinal Products for, Oncologist. 20 (2015) 196–201.

[4] A.G. Ayankojo, J. Reut, A. Öpik, V. Syritski, Sulfamethizole-imprinted polymer on screen-printed electrodes: Towards the design of a portable environmental sensor, Sensors Actuators, B Chem. 320 (2020) 128600.

[5] S. Motia, B. Bouchikhi, E. Llobet, N. El Bari, Synthesis and characterization of a highly sensitive and selective electrochemical sensor based on molecularly imprinted polymer with gold nanoparticles modified screen-printed electrode for glycerol determination in wastewater, Talanta. 216 (2020) 120953.

The Influence of Disintegration Method on Metabolomics Analysis

P-34

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Keywords: *microorganisms, disintegration, metabolomics, NMR*

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

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

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

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

References

[1] R. Bujak, W. Struck-Lewicka, M. J. Markuszewski, and R. Kaliszan, Metabolomics for laboratory diagnostics, J. Pharm. Biomed. Anal. 113 (2015) 108–120.
[2] H. Pearson, Meet the human metabolome, Nature 446 (2007) 8.

Electrochemical Immunosensor for Determination of Glial Fibrillary Acidic Protein Using Screen-Printed Electrodes Modified with Au NPs/L-Cysteine

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Keywords: *Au nanoparticles (AuNPs), Glial Fibrillary Acidic Protein (GFAP), Label-free immunosensor, Screen-printed carbon electrode (SPCE)*

Glial fibrillary acidic protein (GFAP) may serve as a serum marker of traumatic brain injury (TBI) that can be used to monitor biochemical changes in patients and evaluate the response to treatment. GFAP; It is a protein in astrocytes and provides information about the physiological and pathological conditions of astrocytes. An increase of GFAP concentration in serum occurs when the brain is damaged. Recent studies have shown that GFAP is an ideal biomarker in detecting ischemic brain damage and determining astrocyte activity in neonatal hypoxic-ischemic brain damage[1].

Biosensors are important detection technologies in biomedical science, which are defined as a single device platform that identifies targets through biochemical reactions and converts these reactions into electrical, thermal, or optical signals. The use of sensitive and selective analytical methods is essential for the early diagnosis and treatment of the disease. The biosensor offers some advantages such as rapid detection, portability, cheap and user-friendly. Electrochemical sensors based on diverse materials (e.g., nanomaterials, polymers, and biological materials, etc.) are currently in wide use for drugs, proteins, biomarkers, hormones, etc[2].

In this study, the label-free electrochemical impedance immunosensor for the determination of GFAP is reported. A sensitive label-free impedance immunosensor for the detection of GFAP was developed by immobilizing anti-GFAP antibodies via covalent bond onto the activated Au NPs/L-cysteine modified screen-printed carbon electrodes (AuNPs/LC/SPCE). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to study the stepwise assembly of the immunosensor. The use of L-cysteine, Au NPs and greatly enhanced the sensitivity of the immunosensor. The binding of antigens to the immobilized anti-GFAP on the surface of the modified electrode increased the electron-transfer resistance (Ret), which was measured with EIS using 5 mM of $[Fe(CN)_6]^{3-/4-}$ as a redox probe. A linear relationship between Ret and GFAP concentration was obtained and used for the calibration plot. A linear relationship between ∆Rct and GFAP concentration was verified in the range from 1 to 1000 pg.mL^{-1}, with a LOD of 0.51 pg.mL^{-1}. The performance of the immunosensor was validated by evaluating samples with the commercially available enzyme-linked immunosorbent assay method. Therefore, the developed platform can be used in the monitoring of central nervous system injury.

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References

[1] L. Lorente, Biomarkers associated with the outcome of traumatic brain injury patients, Brain Sci. 7 (2017) 1-11. doi:10.3390/brainsci7110142.
[2] O. Hosu, G. Selvolini, C. Cristea, G. Marrazza, Electrochemical Immunosensors for Disease Detection and Diagnosis, Curr. Med. Chem. 25 (2017) 4119–4137.

FPSE Method for Sensitive Analysis of Venlafaxine Molecules in Urine Samples

P-36

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Keywords: *HPLC, Urine Samples, Fabric Phase Sorptive extraction, Venlafaxine*

Depression is an important health problem mainly accompanied by disorders in cognitive, psychomotor and psychophysiological fields, which has a chronic course, can progress with relapses, and causes severe loss of work power and disability. Venlafaxine is the first drug of serotonin (5-HT) and norepinephrine reuptake dual inhibitors, and is also known as a novel antidepressant with unique chemical structure and neuropharmacological activities that differed from other antidepressants [1]. Despite the widespread use of antidepressants, relatively little work has been done on their presence and sensitive analysis in urine samples by fabric phase sorptive extraction and only a few analytical methods exist to detect antidepressants in natural waters.

Within the scope of this thesis, a new enrichment and determination method for Venlafaxine (V) molecules has been developed based on Fabric Phase Sorptive extraction (FSPE) and HPLC-DAD analysis. In proposed method; venlafaxine molecules were drawn to the Sol-Gel Carbowax-20M fabric phase in the presence of pH 10.0 buffer and enriched with ethanol prior to chromatographic determinations by desorbing to a lower volume. The samples which were transferred to HPLC vials by filtration with a 0.45 µm porous PTFE filter before HPLC analysis. Experimental variables such as pH, adsorption time, desorption solvent and its volume were studied and optimized in detail. By using optimal conditions, analytical parameters such as lineer ranges, detection limits, pre-concentation factor for Venlafaxine were calculated by using experimental data.
In the developed method; venlafaxine molecules were analyzed on gradient elution of methanol, acetonitrile and pH:3 buffer with DAD detector at 227 nm wavelength. Limit of detection (LOD) value was calculated as 4.28 ng mL-1. Relative standart deviations (RSD) were below 2.40 % for determinations of model solutions including 300 ng mL-1 venlafaxine. Finally, the developed method has been applied to synthetically urine solutions and wastewater samples with quantitative in recovery experiments.

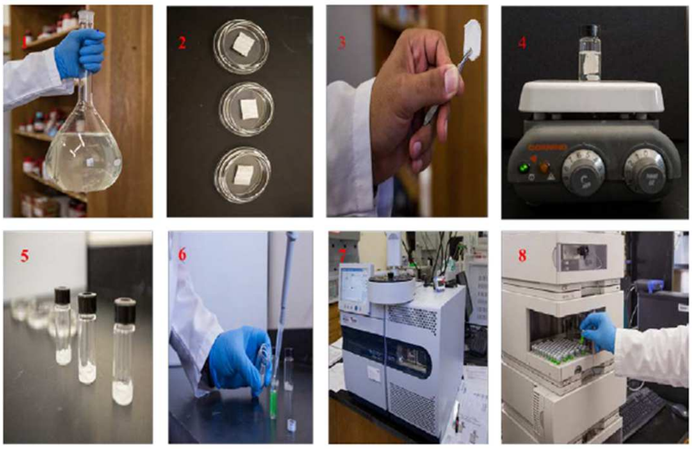

Figure 1. Steps of FSPE [2]

Acknowledgements
This study has been supported by The Scientific and Technological Research Council of Turkey (TUBİTAK) as a 2209-A project with the 1919B011903961 code.

References

[1] S. Shen, C. Zhang, Y. Mao, Determination of venlafaxine and its active metabolite O-desmethylvenlafaxine in human plasma by HPLC fluorescence, Gen Psychiatr. (2018) 31(2) e000010.
[2] A. Kabir, R. Mesa, J. Jurmain, and K. G. Furton, Fabric phase sorptive extraction explained, Separations, 4(2) (2017) 1–21.

Multiresidue Analysis of Antibiotics in Cereals by Liquid Chromatography Triple Mass Spectrometry

P-37

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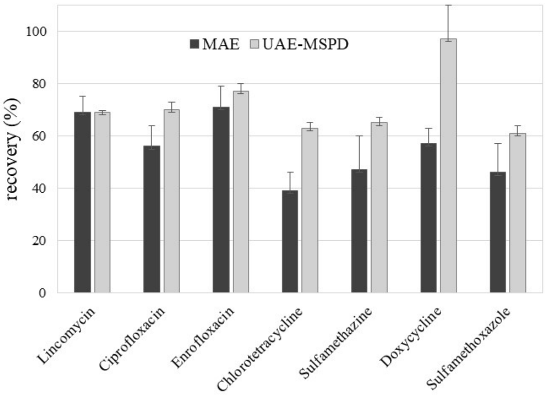
Keywords: *Analysis, Antibiotics, Grains, LC-MS/MS, Uptake*

The main routes of input of antibiotics in the agricultural environment are the use of recycled water for irrigation and the application of sewage sludge, biosolids, and manure to land as soil amendment. As a result of these agricultural practices, antibiotics present in soil can lead to their uptake by plants. Due to the low concentrations expected in plant material, the complexity of the matrices and the characteristics of the antibiotics, there were a lack of validated analytical methods for the determination of antibiotics in crops. Therefore, studies on the levels of antibiotics in cereal samples were scarce in the available literature. The main objective of this study was to develop a selective, sensitive, and efficient analytical method for quantitative determination of 19 antibiotics belonging to different classes in four types of cereal grains.

Firstly, in column-microwave assisted extraction (MAE) was evaluated for the extraction of seven representative compounds from wheat. In this method, a glass sample holder inside the microwave extraction vessel [1] was used to avoid sample transfer and to allow a potential simultaneous clean-up of the cereal extracts. Different organic solvents, sorbents into the glass sample holder, temperature and extraction time were evaluated. Nevertheless, none of them gave quantitative recoveries of the target analytes. As temperatures above 80ºC could not be used using this sample holder, longer extraction times did not increase extraction yields and performing two extraction cycles required the cooling of the sample vessels before collecting the extracts, the improvement of the MAE procedure seemed challenging. Therefore, the combination of matrix solid phase dispersion (MSPD) and ultrasound assisted extraction (UAE) was evaluated in order to overcome the drawbacks of the MAE method. In a general, the extraction of seven antibiotics were higher by UAE-MSPD.



The extraction of the 19 antibiotics from ground wheat grain by UAE-MSPD showed recoveries > 70% for fifteen compounds, but low recoveries (< 11%) were obtained for the other four compounds (tetracycline, erythromycin, tylosin and erythromycin-H_2O). In order to enhance the extraction efficiency for all the compounds, the effect of different parameters, such as the presence of Na_2EDTA or C18 in the dispersion stage, the cleanup by dSPE with PSA, the extraction solvent or the number of UAE cycles, were evaluated. After optimization, the UAE-MSPD method yield recoveries of the target analytes ranging from 73 to 127% for the four cereals analyzed [2]. Compared with methods described for the analysis of antibiotics in cereals, the developed method uses a lower volume of extraction solvent and very good recoveries were obtained for all compounds. The validated method was applied to the analysis of antibiotics in 16 samples of cereals (wheat, barley, oat, and rice) harvested from agricultural fields or purchased from local supermarkets. Enrofloxacin was detected in one rice sample, being the presence of enrofloxacin in cereals or its incorporation into crops from soil or water not previously reported.

Acknowledgements

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References

[1] R.A. Pérez, B. Albero, E. Miguel, C. Sánchez-Brunete, Determination of parabens and endocrine-disrupting alkylphenols in soil by gas chromatography-mass spectrometry following matrix solid-phase dispersion or in-column microwave-assisted extraction: a comparative study. Anal Bioanal Chem. 402 (2012) 2347–57J. van der Geer, J.A.J. Hanraads, R.A. Lupton, The art of writing a scientific article, J. Sci. Commun. 163 (2010) 51-59.

[2] B. Albero, J.L. Tadeo, E. Miguel, R.A. Pérez Rapid determination of antibiotic residues in cereals by liquid chromatography triple mass spectrometry. Anal Bioanal Chem. 411 (2019) 6129-6139.

Determination of Seven Representative Antibiotics in Lettuce to Monitor Their Uptake

P-38

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Keywords: *Analysis, Lettuce, LC-MS/MS, Pharmaceuticals, UAE*

The main entry routes of antibiotics into the environment are the application of organic residues as soil amendment or fertilizer, and the use of recycled water for irrigation. Once antibiotics are released into the environment, their behavior and uptake by plants depends not only on their physicochemical properties, but also on the characteristics of soil, the crop and its growing conditions. Root uptake is expected to be an important route of plant exposure to antibiotics.

The multiresidue analysis of antibiotics in vegetables presents many difficulties due to the complexity of the matrix and the different physicochemical properties of these compounds. Thus, different methods for the determination of pharmaceutical and personal care products in plant tissues have been reported, but for some of the target compounds the relative recovery results were < 60% [1-5]. So, the aim of this study was to develop a selective, sensitive, and efficient analytical method for the quantitative determination of seven representative antibiotics belonging to different classes (fluoroquinolones, tetracyclines, sulfonamides and lincosamides) in lettuce. Therefore, an analytical method based on ultrasound-assisted extraction (UAE) for the determination of seven antibiotics in lettuce was developed.

Firstly, different parameters of the extraction of antibiotics spiked in thawed lettuce were optimized but recovery yields for sulfonamides did not exceed 42%. But when the extraction was carried out from lyophilized samples, using similar conditions to the thawed samples, the extraction of the two sulfonamides clearly improved.

The developed method was applied to evaluate antibiotic uptake by lettuce grown in pots fertilized with composted poultry litter doped with a mixture of antibiotics to reach a final concentration of 2.5 µg/g in soil. Lettuce were harvested after 21, 36 and 55 days. Five of the seven studied antibiotics were found in all samples. The highest uptake was found for lincomycin (51 ng/g fresh weight) followed by sulfamethoxazole (44 ng/g fresh weight) and sulfamethazine (21 ng/g fresh weight) in lettuce harvested after 21 days. An important decrease of their levels was observed after 36 days, but these levels remained similar after 55 days. Although levels found in lettuce were low, the presence of antibiotics demonstrates the need for further assessing food safety risks related with the use of soil amendments or irrigation water contaminated with antibiotics.

In order to improve the extraction efficiency, modifications in the initial extraction solvent, acetonitrile-water (80:20, v/v), were assayed, such as the extraction with aqueous formic acid instead of water, a decrease in the proportion of organic phase (acetonitrile-aqueous formic acid 0.5% (60:40, v/v), or the addition of methanol in the extraction solvent (acetonitrile-methanol-aqueous formic acid 0.5% (65:15:20, v/v/v). Thus, when two extractions of 0.2 g of lyophilized lettuce were carried out using acetonitrile-methanol-formic acid 0.5% (65:15:20, v/v/v) and UAE during 15 min, followed by dispersive solid-phase extraction (dSPE) with 1 g of C18 for cleanup, the recovery results obtained were satisfactory (> 70%) for most of the compounds [6].

The validated method was applied to evaluate antibiotic uptake by lettuce grown in pots fertilized with composted poultry litter doped with a mixture of antibiotics. Lettuces were harvested at three different periods of time (after 21, 36 and 55 days) and the plant analyses showed that five of the seven studied antibiotics were found in all samples. The highest uptake was found for lincomycin followed by sulfamethoxazole and sulfamethazine in lettuce harvested after 21 days. These levels are low but its presence highlights the need for further assessing food safety risks related with the use of soil amendments or irrigation water contaminated with antibiotics.

Acknowledgements

Authors wish to thank the Spanish Ministry of Economy, Industry and Competitiveness for financial support, project (RTA2014-00012C03).

References

[1] X. Wu, L.K. Dodgen, J.L. Conkle, J Gan, Plant uptake of pharmaceutical and personal care products from recycled water and biosolids: A review. Sci. Total Environ. 536 (2015) 655–666.

[2] F. Hu, K. Bian, Y. Liu, Y. Su, T. Zhou, X. Song, L. He, Development of a modified QUick, Easy, CHeap, Effective, Rugged and Safe method for the determination of multi-class antimicrobials in vegetables by liquid chromatography tandem mass spectrometry. J. Chromatogr. A 1368 (2014) 52–63.

[3] Y.H. Chuang, Y. Zhang, W. Zhang, S.A. Boyd, H. Li, Comparison of accelerated solvent extraction and quick, easy, cheap, effective, rugged and safe method for extraction and determination of pharmaceuticals in vegetables. J. Chromatogr. A 1404 (2015) 1–9.

[4] J.B. Sallach, D. Snow, L. Hodges, X. Li, S. Bartelt-Hunt, Development and comparison of four methods for the extraction of antibiotics from a vegetative matrix. Environ. Toxicol. Chem. 35 (2016) 889–897.

[5] Đ. Tadić, V. Matamoros, J.M. Bayona, Simultaneous determination of multiclass antibiotics and their metabolites in four types of field-grown vegetables. Anal. Bioanal. Chem. 411 (2019) 5209–5222.

[6] B. Albero, J.L. Tadeo M.M. Delgado, E. Miguel, R.A. Pérez Analysis of multiclass antibiotics in lettuce by liquid chromatography–tandem mass spectrometry to monitor their plant uptake Molecules 24 (2019) 4066.

Fabrication of an Electrochemical Sensor for Determination of a Serotonin 5-HT3 Receptor Antagonist

P-39

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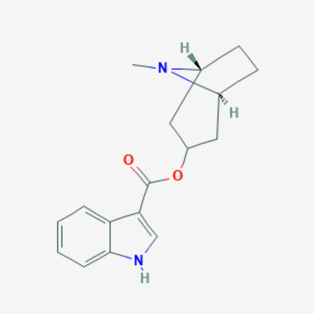
Keywords: *Tropisetron, 1-(2,4-dinitrophenyl)-dodecanoylthiourea, ZnO, screen printed electrode, electrochemical sensor*

Tropisetron (TRP) is an indole derivative with antiemetic activity. As a selective serotonin receptor antagonist, tropisetron competitively blocks the action of serotonin at 5HT3 receptors, resulting in suppression of chemotherapy-and radiotherapy-induced nausea and vomiting. Tropisetron appears to be well tolerated with the most frequently reported adverse effect being a headache. Extrapyramidal side effects are rare upon using tropisetron [1].

Electrochemical measurements are user-friendly, efficient, cheaper, and easier as compared to other techniques like spectroscopy and chromatography. Several strategies are employed to improve the efficiency of sense. One of the strategies is the use of nanomaterial as a recognition element, catalyst, or conductor for the amplification of signals for the detection of analytes. Several techniques have been employed for the study of TRP such as high-performance liquid chromatography (HPLC), capillary electrophoresis, liquid chromatography (LC) coupled with mass spectrometry. Literature research reveals that the electrochemical investigation of TRP at a bare or modified electrode is an unexamined matter. In this work, TRP was investigated using electrochemical techniques for the first time [2,3].

An electrochemical sensor was improved by using surfactant 1-(2,4-dinitrophenyl)-dodecanoylthiourea (DAN) along with ZnO as a modifier on the screen-printed electrode (SPE) for the determination of TRP. The designed sensor for the determination of TRP was characterized by electrochemical techniques such as impedance spectroscopy, cyclic voltammetry (CV), and square wave voltammetry (SWV). For optimization, the effect of several factors such as scan rate, the concentration of the modifier, accumulation time, pH, supporting electrolytes, effect of deposition potential was investigated. The limit of detection was found to be 83 pM using DAN/ZnO/SPE. The reasonable percentage recoveries with less than 2% RSD values were obtained for the human serum sample analysis ensured the validity of the proposed sensor. Furthermore, the designed sensor shows exceptional stability, sensitivity, accuracy, and reproducibility, which suggests our proposed sensor is a potential candidate for the detection of TRP in its working samples. Theoretical study of modifier ZnO/DAN with TRP was carried out using the Density-Functional Tight-Binding (DFTB) method by ADF software and the negative interaction energy between the modifier and target analyte favors the experimental findings.



Scheme 1. Chemical Structure of Tropisetron

References

[1] M. Doulache, N.K. Bakirhan, B. Uslu, B. Saidat, M. Trari, S.A. Ozkan, Simple and sensitive adsorptive stripping voltammetric assay of granisetron from its dosage form by platinum nanoparticles modified electrodes, Sens. Actuators B-Chem, 251 (2017) 572-582.

[2] N.K. Bakirhan, M.S.B. Celik, H. Celik, B. Uslu and S.A. Ozkan, Electrochemical Approach on Mechanism of an Oral Progestin in Aqueous Media and its Fully Validated Detection via a Carbon□Metal Based Composite Sensor, Electroanalysis, 30 (2018) 2273-2283.

[3] A. Zahid, A. Shah, F.J. Iftikhar, A.H. Shah and R. Qureshi, Electrochim. Acta, Development of surfactant based electrochemical sensor for the trace level detection of mercury, 235 (2017) 72-78.

Development of a Liquid-liquid Extraction Method for the Determination of Short Chain Fatty Acids from Bacteria Culture

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Keywords: *Short-chain fatty acids, Lactic acid, Liquid-liquid Extraction, HPLC-UV*

In this study, we present an extraction and a sensitive separation method that can be used for the detection of three short-chain fatty acids (SCFAs) and lactic acid (LA) produced by bacteria in a medium.

All matrix-matched and real samples were extracted with a modified version of Baere's extraction method (2013) [1]. The liquid-liquid extraction procedure was carried out with tert-Butyl methyl ether and back extraction with sodium hydroxide was applied in the last step.

The chromatographic separation was performed on a XBridge C18 (4.6 mm x 250 mm, 5 µm) analytical column, and the same type guard column (4 mm × 3 mm) was used. 15 mM phosphate buffer (pH 2.1) and acetonitrile (70:30, v/v) were used as mobile phase. The analysis was performed by adjusting the instrument settings to a flow rate of 1 mL.min -1, detector wavelength 210 nm, column temperature 10° C, and an injection volume of 5 µL. Gradient elution was performed for separation.

Calibration curves were created for all analytes and correlation coefficients were between 0.9943–0.9995. Limits of detection and quantification ranged from 0.12 to 0.5 mM and 0.37 to 1.5 mM, respectively.

The modified extraction and separation method were validated for parameters such as selectivity, linearity, LOD, LOQ, precision, accuracy specified in the ICH guidelines [2].

As a result, it has been shown that the analysis of short-chain fatty acids in the culture filtrate supernatant can be successfully performed with this study we have presented. In addition, this method can be used for the quantitation of SCFAs (acetic, propionic, butyric acids) and LA produced by bacteria species isolated from various media.

Acknowledgements

References

[1] De Baere S, Eeckhaut V, Steppe M, De Maesschalck C, De Backer P, Van Immerseel F, Croubels S. Development of a HPLC-UV method for the quantitative determination of four short-chain fatty acids and lactic acid produced by intestinal bacteria during in vitro fermentation. J Pharm Biomed Anal. 80 (2013) 107-115.
[2] CPMP/ICH/381/95 - ICH harmonised tripartite guideline - Validation of Analytical Procedures: Text and Methodology Q2(R1). 2014. https://www.ema.europa.eu/en/ich-q2-r1-validation-analytical-procedures-text-methodology (Accessed 4 October 2020).

A Nanocomposite Magnetic Core-Shell Material for Sensitive Analysis of Quercetin in Tea Samples by HPLC

P-41

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Keywords: *HPLC, Magnetic Solid phase extraction, Tea Samples, Quercetin*

Antioxidant activities of various polyphenolic compounds as flavonoids are well known in edible plants, vegetables, wine, fruits, and herbal tea. Analysis of flavonoids in natural sources has attracted much attention by many researchers from different area. Quercetin is one of the most active and common compounds in flavonoid family. This work was aimed to synthesis and characterization of magnetic core-shell multiwalled carbon nanotube@nanodiamond (MWCNT@ND) nanocomposite for the sensitive solid-phase extraction of quercetin prior to detection with reversed-phase liquid chromatography with UV–visible diode array detector (HPLC-DAD) [1].

A new magnetic core-shell multiwalled carbon nanotube@nanodiamond nanocomposite was synthesized, characterized and used as magnetic solid-phase extraction material. The usability of material was checked on the separation and pre-concentration of quercetin in tea samples by magnetic solid-phase extraction and high-performance liquid chromatography with diode array detector system. There was a linear relationship between chromatographic area and concentration of quercetin in the range of 5.0–600 ng mL^{-1} . The limit of detection and quantification limits were 1.46 and 4.91 ng mL^{-1}, respectively. The developed method has been applied to determine quercetin at trace levels in tea samples.

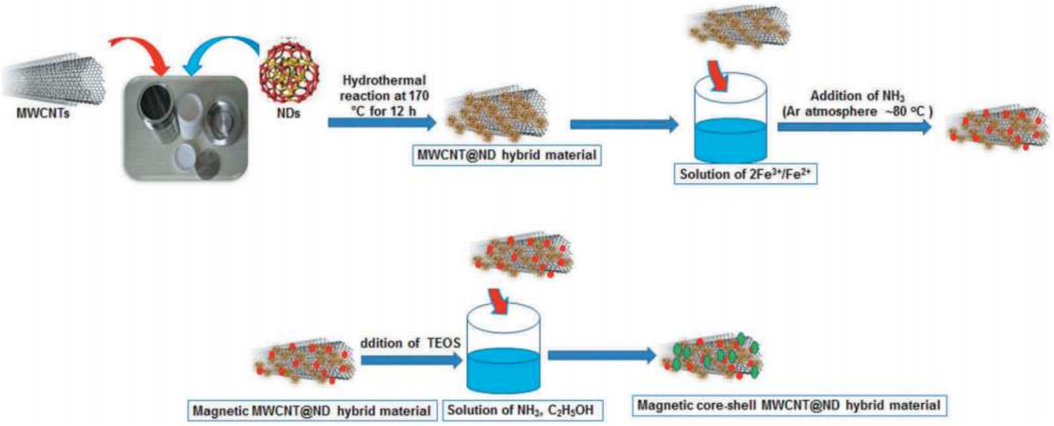

Figure 1. Graphical abstract of the proposed method [2]

References

[1] S.R. Banforuzi, M.R. Hadjmohammadi, Two-phase hollow fiber-liquid microextraction based on reverse micelle for the determination of quercetin in human plasma and vegetables samples. Talanta (2017) 173: 14–21.

[2] S. Ulusoy, H.I. Ulusoy, Z. Erbas, E. Yilmaz, M. Soylak, Trace analysis of quercetin in tea samples by HPLC-DAD system by means of a new nanocomposite including magnetic core-shell, Separation Science and Technology (2020) 55 (11) 2025–2036.

Native Fluorescent Natural Deep Eutectic Solvents for Green Sensing Applications: Curcuminoids in *Curcuma longa* Powder

P-42

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Keywords: *AGREE Metric; Curcuminoids; Fluorescencet NADES; Single-step extraction; Ultrasound probe.*

Natural deep eutectic solvents are a trending topic in Green Chemistry. These solvents present high solubilization capacity, reusability, tunable properties, simple preparation, biodegradability, safety, high availability and low cost, making them excellent candidates for analytical applications [1]. In this work, a new family of fluorescent eutectic systems is described, being the fluorescence property unknown and unused so far. For this purpose, a novel preparation method using an ultrasound probe was employed, by means of an innovative single step procedure, that included the preparation of FCH (fructose, citric acid and water, 1:1:5 molar ratio) and the extraction/determination of curcuminoids from *Curcuma longa* powder (Figure 1). This methodology was successfully carried out employing a portable and inexpensive 3D printed fluorometer and a smartphone [2]. In this way, extraction efficiencies between 90-106%, relative to the NIST reference method, were obtained [3], in just 3.40 min. Besides, the greenness of the new methodology was evaluated employing the AGREE Metric [4], showing that the developed approach is more than 2.5 times greener than previously published works for curcuminoid determination. This groundbreaking procedure is robust, versatile, simple to implement, does not require sophisticated apparatus or instruments in the detection step and mainly, agrees with GAC principles [5].

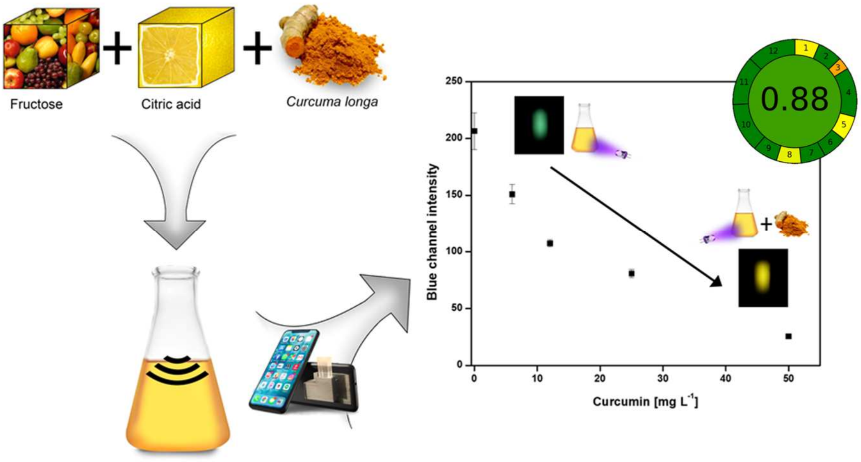

Figure 1. Graphical representation of the proposed innovative single-step entirely green procedure for the preparation of new fluorescent NADES and analyte extraction.

References

[1] M. Espino., M. de los Ángeles Fernández, F. J. V.Gomez, M. F. Silva, Natural Designer Solvents for Greening Analytical Chemistry. TrAC Trends Anal. Chem. 76 (2016) 126–136.
[2] E. Vidal, A. S. Lorenzetti, M. Á. Aguirre, A. Canals, C. E. Domini, New, Inexpensive and Simple 3D Printable Device for Nephelometric and Fluorimetric Determination Based on Smartphone Sensing. RSC Adv. 10 (2020) 19713–19719.
[3] National Institute of Standards & Technology. Certificate of Analysis, Standard Reference Material 3299. 2019, No. September, 2–5.
[4] F. Pena-Pereira, W. Wojnowski, M. Tobiszewski, AGREE - Analytical GREEnness Metric Approach and Software. Anal. Chem. 92 (2020) 10076–10082.
[5] S. Armenta, F. A. Esteve-Turrillas, S. Garrigues & M. de la Guardia, Green Extraction Techniques: Principles, Advances and Applications, Vol 76, 1s., Elena Ibanez and Alejandro Cifuentes, Ed., Elsevier, 2017.

Voltammetric Determination of Anticancer Drug Axitinib Using Boron-Doped Diamond Electrode

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Keywords: *Axitinib, Boron-doped diamond electrode, Pharmaceutical dosage forms, Voltammetry*

Tyrosine kinase is a significant intermediary that triggers various types of cancer, such as kidney and thyroid. The vascular endothelial growth factor receptor (VEGFR) tyrosine kinases 1, 2, and 3, play a role in the progress of various cancers. Axitinib (AXT), a second-generation targeted drug, is a potent and selective inhibitor of VEGFR tyrosine kinase.

A voltammetric technique has been developed for the quantification of AXT using boron-doped diamond electrode. The oxidation mechanism of AXT was investigated by cyclic and differential pulse in the supporting electrolytes which acetate, phosphate, Britton Robinson buffers and sulfuric acid solutions in the pH range between 0.1 and 7.0. The scan rate studies of AXT was performed by cyclic voltammetric technique in pH 0.1 M H_2SO_4. According to the scan rate studies, the oxidation reaction of the AXT was found to be irreversible and investigated as details and compared with some model compounds and drugs. The log Ip–log v slopes was found as 0.5575. According to this result, the electrochemical reaction was found as diffusion controlled process.

A simple, sensitive, and low-cost voltammetric method using boron-doped diamond electrode was developed for the determination of AXT. AXT provided an irreversible oxidation peak at a potential of 0.912 V versus Ag/AgCl/KCl (3 mol L^{-1}) electrode in acetate buffer solution (pH 3.7). Under optimal experimental conditions, differential pulse voltammetry (DPV) was used for the determination of AXT. DPV methodology was proposed for the sensitive determination of AXT in a linear concentration range from 0.60 μM to 80 μM, with a detection limit of 0.368 nM and a good repeatability (RSD of 0.285 %). The developed methods were applied to analysis of the human urine, synthetic serum samples and tablet dosage form with the recoveries 100.38 %, 100.29 %, and 101.25 %, respectively.

The developed methods can be used with the desired accuracy and precision for routine control analysis of biological and pharmaceutical samples. The response time for sensing, greener, simplicity of sample pre-treatment is the advantage of developed methods.

References

[1] A. Arora, E.M. Scholar, Role of tyrosine kinase inhibitors in cancer therapy, J. Pharmacol. Exp. Ther. 315 (2005) 971–979.

[2] M. Gross-Goupil, L. François, A. Quivy, A. Ravaud, Axitinib: A review of its safety and efficacy in the treatment of adults with advanced renal cell carcinoma, Clin. Med. Insights Oncol. 7 (2013) 269–277.

Andrew+ Automated Oasis 2x4 Mixed Mode Sorbent Selection SPE Protocol

P-44

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Keywords: *Andrew+, Automation, Method Development, Mixed mode, SPE, Oasis.*

Liquid Chromatography Mass Spectrometry (LC-MS) analysis of complex biological samples often requires extensive sample cleanup to remove the undesirable components from the sample matrix, which otherwise will inadvertently affect the analysis; resulting in MS ion signal suppression or enhancement. Mixed mode solid phase extraction (SPE) is a commonly used sample preparation technique for LC-MS analysis to attain greater selectivity. However, developing mixed mode SPE methods can be a challenging task. Not knowing where to start or which sorbents to choose can be daunting. Furthermore, adding to the complexity, most mixed mode SPE workflows involve several steps of pipetting and transfer of samples, reagents and solvents. Automation of these pipetting and transfer workflows using expensive liquid handlers often involve complex programming, needing expert, trained and dedicated personnel to perform the task; while performing workflows manually can be extremely tedious and prone to errors, requiring good analytical skills for a reproducible result. In this work an automated SPE workflow for a quick, reliable and reproducible SPE mixed mode sorbent selection method development, using Andrew+ pipetting robot, connected and operated using OneLab, an easy to use browser-based interface is described in this work. To demonstrate the ease of automated SPE method development; analytes were extracted from spiked human blood plasma following the Oasis® 2x4 method development protocol using Waters™ Oasis method development 95 well µElution plate.

References

[1] Oasis Sample Extraction Products:Methodology. Waters Application Note 720003679, September 2010.

Enhancing Laboratory Throughput Using Fully Automated High-Capacity Sorptive Extraction

P-45

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Keywords: *Automation; High-capacity sorptive extraction; Laboratory throughput; Sample Preparation*

The application of polydimethylsiloxane (PDMS) as an extraction medium for the enrichment of both apolar and polar analytes from gaseous headspace and liquid samples has recently found wide acceptance for a range of applications. By using a large amount of sorptive phase, volatile and semi-volatile organic compounds can be efficiently enriched and compared to solid-phase microextraction, a significant increase in sensitivity is achieved.

Until recently, high-capacity sorptive extraction has been a manual method in which the user was required to remove the phase, clean, dry and place it into a thermal desorption unit. This made the technique time-consuming resulting in low sample throughput, a concern for many analytical laboratories, especially those dealing with a high volume of samples, in particular, critical samples that require a fast turnaround time. The need to streamline processes while removing the human error factor is extremely important.

High-capacity sorptive extraction can overcome these limitations and offers high sample throughput, thanks to full automation of the entire workflow using gold-standard robotics and the patented ‘grab and release’ technology on Centri. One valuable additional feature of the extraction technique is sample management; a six-place integrated sample agitator combined with the patented technology allows simultaneous extraction of multiple sample vials at any one time (known as ‘prep-ahead’ mode), allowing for just-in-time sample preparation, leading to higher throughput and faster time to results..

A Straightforward and Semiautomated Membrane-based Method for the Determination of Cocaine and its Metabolites in Urine Samples Using LC-ESI-QTOF-MS

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Keywords: *Automation, Drugs of Abuse, HFRLM, Sample Preparation, 96-well plate.*

Cocaine (COC) is an alkaloid psychostimulant extracted from *Erythroxylum coca* leaves which is mainly used due to its transient euphorigenic effects. Cocaine abuse can lead to dependence and its chronical use promotes a variety of effects including paranoia, disorientation and sudden cardiac death [1]. In this study, a novel and straightforward analytical methodology was proposed for the determination of cocaine (COC) and its main metabolites benzoylecgonine (BZE) cocaethylene (CE) and hydroxy-cocaine (COC-OH) in urine samples. This approach consisted of a semiautomated configuration based on hollow-fiber renewal liquid membrane extraction (HFRLM) coupled to a 96-well plate system proposed, for the first time, to analyze complex biological samples such as urine. The analytical determinations were performed using ultra-high performance liquid chromatography coupled to quadrupole time-of-flight-mass spectrometry (LC-ESI-QTOF-MS). The analytical methodology was fully optimized through Doehlert and simplex-centroid designs, and univariate approaches. Polypropylene membranes of 1 cm length were inserted in the pins of an extraction blade combined with a 96-well plate system and its pores were filled with hexane:dichloromethane:ethyl acetate (1:1:1 v/v/v) for 180 s; moreover, 20 µL of this mixture was added to the sample to allow for a renewable liquid membrane. The extraction step was carried out by keeping the blades immersed in vials containing 1.5 mL of diluted urine adjusted at pH 10 with 10% (w/v) of Na_2CO_3 during 20 min, followed by liquid desorption with 100 µL of acetonitrile. Finally, the extract was dried under N_2 stream and resuspended with 20 µL of ultrapure water and injected in the chromatographic system. Using this approach, satisfactory results were achieved for the analytical parameter of merit as shown in Table 1.

Table 1. Analytical parameters of merit obtained with the HFRLM/96 well-plate methodology [2].

Analyte	Linear Equation	Slope Standard Deviation	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	Linear Range (ng mL^{-1})	R^2
COC	y = 0.0157x + 0.0194	± 0.00035	1.5	5	5 - 80	0.9985
BZE	y = 0.003x + 0.0146	± 0.00019	15.1	50	50 - 500	0.9875
CE	y = 0.0274x + 0.0503	± 0.00050	1.5	5	5 - 80	0.9986
COC-OH	y = 0.0066x + 0.0279	± 0.00022	1.5	5	5 - 80	0.9953

Moreover, intra-day precision (n=5) ranged from 1.6 to 13.5% and inter-day precision (n=5) varied from 2.2 to 17.5%. Relative recoveries ranged from 70.7% (± 3.9%) to 124.1% (± 0.7%). The methodology was applied in urine samples obtained from *Instituto Geral de Perícias* – RS, Brazil, according to the Ethics Approval number 00913718.3.0000.0121, and cocaine or its metabolites were determined in nine out of eleven samples examined. Only one sample exhibited concentrations lower than LOQ for the compounds studied. Other important factor to be noticed is regarding the concentration of BZE, which is the main metabolite of cocaine that can be found in urine. Generally, the concentration of BZE in urine is higher than other metabolites. In samples containing concentrations higher than LOQ, the found concentrations varied from 132.3 to 337.9 ng mL^{-1} for BZE; from 6.2 to 25.9 ng mL^{-1} for COC; from 5.9 to 16.8 ng mL^{-1} for CE; and from 5.7 to 12.8 ng mL^{-1} for COC-OH.

The analytical methodology based on the use of hollow fiber renewable liquid membrane extraction (HFRLM) coupled to 96-well plate system consisted of an environmentally-friendly sample preparation procedure in which few microliters of organic solvent were used for the extraction/desorption of the analytes, and LC-ESI-QTOF-MS allowed for accurate and very satisfactory analytical results. In addition, this technique provided high-throughput since 96 samples can be extracted simultaneously.

Acknowledgements

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References

[1] M.J. Valente, F. Carvalho, M.L. Bastos, M. Carvalho, P.G Pinho, Development and validation of a gas chromatography/ion trap-mass spectrometry method for simultaneous quantification of cocaine and its metabolites benzoylecgonine and norcocaine: Application to the study of cocaine metabolism in human primary cultured renal cells. J. Chromatogr. B. 878 (2010) 3083-3088.

[2] G. Mafra, L. Birk, C. Scheid, S. Eller, R. Brognoli, T.F. Oliveira, E. Carasek, J. Merib, A straightforward and semiautomated membrane-based method as efficient tool for the determination of cocaine and its metabolites in urine samples using liquid chromatography coupled to quadrupole time-of-flight-mass spectrometry. J. Chromatogr. A. 1621 (2020) 461088.

Trace Sibutramine Determination in Herbal Slimming Products

P-47

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Keywords: *HPLC, Herbal slimming products, Magnetic solid phase extraction, Sibutramine*

Sibutramine (SBM) is a synthetic serotonin-noradrenalin re-uptake inhibitor, structurally related to amphetamines. However, some unscrupulous manufacturers are mixing Sibutramine with food supplements and slimming products sold illegally through outlets online and in the black market. In the interests of consumer safety, a simple and sensitive method is therefore needed to effectively screen and detect Sibutramine in these products [1].

Within the scope of this study, a new enrichment and determination method, which includes HPLC-DAD analysis after Magnetic Based Solid Phase Micro Extraction (MSPE), has been developed for tracing Sibutramine molecules, which are widely used especially in slimming products, at trace level. In this proposed method; The sibutramine molecules are enriched by using the magnetic phase synthesized in our laboratory as a sorbent in the presence of pH: 8.0 buffer and further enriched by desorption to acetonitrile/methanol mixture before chromatographic determinations. Before the analysis, samples transferred to HPLC vials by filtering with 0.45 µm porous PTFE filter were placed in the HPLC device and analytical parameters such as linear interval, enrichment factor and determination limit were determined after optimizing experimental variables such as interaction time, desorption solvent, pH. In the developed method; sibutramine molecules were analyzed on isocratic elution of acetonitrile (40) and pH:3 buffer (60) with DAD detector at 223 nm wavelength. Limit of detection (LOD) value was calculated as 1.43 ng mL^{-1}. Relative standard deviations (RSD) were below 3.20 % for determinations of model solutions including 200 ng mL^{-1} of sibutramine. Finally, the developed method has been applied to herbal slimming tea samples with quantitative in recovery experiments.

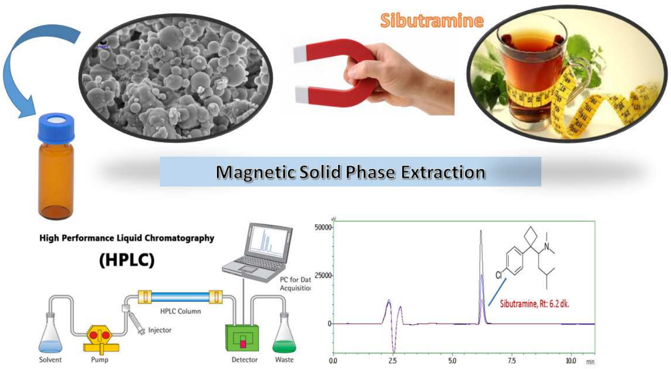

Figure 1. Graphical Abstract of the proposed method

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References

[1] S. Kiattisak, P. Warakorn, W. Limbut, Adsorption and determination of sibutramine in illegal slimming product using porous graphene ink-modified electrode, Talanta (2020) 212 120788.

Detection of Cationic Surfactants in Disinfectants and Antiseptics by New Direct Potentiometric Surfactant Sensor

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Keywords: *Antiseptic, Cationic surfactant, Potentiometry, Personal care products.*

Cationic surfactants are used as antiseptics, disinfectants, bactericides, corrosion inhibitors and cleaning agents in home products and professional products in hospitals, industry, as oilfield chemicals and in agronomy. Cationic surfactants have a positively charged head which allows them to stick to negatively charged surfaces, preventing the electrostatic repulsion and also acting as textile softeners. Nonionic surfactants are amphipathic molecules that contain a lipophilic part, usually long alkyl chain or fatty acid, and a hydrophilic portion such as ethylene oxide chain of various length and thus, are nonionizable in water **[1]**. Nonionic surfactants enhance the cleaning properties of cationic surfactants **[2]**. Formulations of cationic with nonionic surfactants are common in many personal care products and pharmaceuticals **[3,4]**.

A newly synthesized cationic surfactant based on imidazole was used as counter ion to tetraphenylborate (TPB) to form the ionophore implemented in potentiometric surfactant sensor to detect cationic surfactants in commercial personal care products and antiseptics. The surfactant sensor showed good response characteristics to cationic surfactants usually used in commercial product formulations. with Nernstian slope from 57.1 to 59.1 mV/decade. The lowest limit of detection was obtained for cetylpyridinium cationic surfactant (1.1×10^{-6} M). Sensor exhibited fast dynamic response to dodecyl sulfate (DDS) and TPB, low interference influence and low pH influence. Ethoxylated nonionic surfactants had a significant influence on cationic surfactant detection with surfactant sensor in terms of end-point detection and shape and size of direct potentiometric titration curves. The sensor was successfully applied for the quantification of technical grade cationic surfactants and twelve products commercial personal care and antiseptic products with good agreement with referent two-phase titration method.

References

[1] M. Sak-Bosnar, D. Madunić-Čačić, N. Sakač, O. Galović, M. Samardžić, Z. Grabarić, Potentiometric Sensor for Polyethoxylated Nonionic Surfactant Determination. Electrochim. Acta 55 (2009) 528–534.

[2] K. Ogino, M. Abe, Mixed Surfactant Systems, second ed., Marcel Dekker, Inc., New York, 1993.

[3] R. Kawai, M. Niki, S. Yada, T. Yoshimura, Surface Adsorption Properties and Layer Structures of Homogeneous Polyoxy-ethylene-Type Nonionic Surfactants in Quaternary-Ammonium-Salt-Type Amphiphilic Gemini Ionic Liquids with Oxygen- or Nitrogen-Containing Spacers, Molecules 25 (2020) 4881-4891.

[4] H. Natsheh, E. Touitou, Phospholipid Vesicles for Dermal/Transdermal and Nasal Administration of Active Molecules: The Effect of Surfactants and Alcohols on the Fluidity of Their Lipid Bilayers and Penetration Enhancement Properties, Molecules 25 (2020) 2959-3001.

Comparison of Headspace Solid-Phase Microextraction High Capacity Fiber Coatings for Untargeted Analysis of Beer Volatiles Using GC-MS/VUV

P-49

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Keywords: *Absorption spectroscopy, Beverage analysis, Multivariate classification, SPME Arrow*

Despite the same basic ingredients used in brewing, there is a significant variation in beer styles. With the rapid increase in craft brewing, beer styles have become even more numerous and complex in the recent past. A GC-MS/VUV (post-column split for dual detection) instrument with headspace high capacity SPME was used to investigate 21 different beers which represent three beer styles - India pale ales, blondes, and hefeweizens. Headspace solid-phase microextraction (SPME) is one of the most frequently used extraction techniques for the analysis of volatile organic compounds (VOCs) in complex matrices [1]. High capacity SPME fibers possess a larger extraction phase volume, increasing the sensitivity of the technique and therefore improving the extraction approach [2]. Since results from untargeted studies can be affected by the sorbent material used, the extraction performances of three high capacity SPME fibers, i.e., polydimethylsiloxane, polydimethylsiloxane/carbon wide range, and polydimethylsiloxane/carbon wide range/divinylbenzene, were evaluated. The extraction conditions, i.e., incubation time, extraction time, extraction temperature, and desorption time, were optimized using a central composite design. Good reproducibility (<10% RSD) was obtained for each high capacity fiber using both GC and VUV detectors. The PDMS/CarWR fiber exhibited the highest reproducibility with a 5.2%RSD using the MS for detection and 6.4%RSD using the VUV. For most of the compound classes detected in the beer samples, higher extraction yields were obtained using the diphasic and triphasic fibers. However, similar clustering was observed with the three fiber chemistries, indicating similar extraction performances for the three fiber types.The tandem MS/VUV detection coupled with GC separation proved to be particularly valuable for compound identification, especially for isomers and compounds with similar structures. The evaluation of VUV detection for untargeted analysis led to similar performances as MS detection. Both the VUV and the MS were able to effectively differentiate between beer styles using principal component analysis. In addition, the use of 3 different statistical approaches universally identified 12 of the components most influential in distinguishing the three beer styles (e.g., β-myrcene, linalool, isopentyl acetate, 2,4-di-tert-butylphenol). This is the first reported evaluation of VUV detection and the first comparison of simultaneous VUV and MS detection for untargeted classification of complex mixtures using GC.

References

[1] É.A. Souza-Silva, E. Gionfriddo, J. Pawliszyn, A critical review of the state of the art of solid-phase microextraction of complex matrices II. Food analysis, TrAC - Trends Anal. Chem. 71 (2015) 236–248.
[2] A. Kremser, M.A. Jochmann, T.C. Schmidt, PAL SPME Arrow - Evaluation of a novel solid-phase microextraction device for freely dissolved PAHs in water, Anal. Bioanal. Chem. 408 (2016) 943–952.

LC-GC×GC-ToFMS/FID: A Powerful Technique for MOSH and MOAH Quantification and Characterization

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Keywords: *Comprehensive two-dimensional gas chromatography, LC-GC×GC, Mineral oil aromatic hydrocarbons, Mineral oil saturated hydrocarbons, quantification.*

Mineral oil hydrocarbons (MOHs) are generally classified into mineral oil saturated and aromatic hydrocarbons with different toxicological relevance and analytical challenges. Among the many challenges, data interpretation and integration represent an important source of uncertainty in the results provided by different laboratories leading to a variation evaluated on the order of 20%. The use of multidimensional comprehensive gas chromatography (GC×GC) has been proposed to support the data interpretation but the integration and the reliability of the results using this methodology have never been systematically evaluated. The aim of this work was to assess the integration and quantification performances of a two-dimensional (2D) software. The data were generated using a novel, completely automated platform, namely LC-GC×GC coupled to dual detectors, i.e., time-of-flight mass spectrometer (MS) and flame ionization detector (FID). From a systematic study of the failures of the two-dimensional quantification approach a novel solution was proposed for simplifying and automating the entire process. The novel algorithm was tested on ad hoc created samples (i.e. a paraffin mixture added of n-alkanes) and real-world samples proving the agreement of the results obtained by GC×GC and the traditional mono-dimensional (1D) approach. Moreover, the benefits of using an entirely integrated platform were emphasized, particularly regarding the identity confirmation capability of the MS data, which can be easily translated into the 2D FID quantification feature [1].

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References

[1] G. Bauwens, S.Pantó, G. Purcaro, J. Chorlatography A, 2021 (under revision)

Pristine and Functionalized Multi-Walled Carbon Nanotubes as Adsorbent Material for Solid-Phase Extraction of Multi-Class Organic Micropollutants

P-51

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Keywords: *Contaminants of emerging concern; carbon nanotube cartridges; green solvent; priority substances; ultra-high performance liquid chromatography-tandem mass spectrometry.*

In the present work, original and functionalized multiwalled carbon nanotubes (MWCNTs) were investigated as adsorbent material in solid-phase extraction (SPE) cartridges for extraction of 8 organic micropollutants with different p*K*a and polarity range (acetamiprid, atrazine, carbamazepine, diclofenac, isoproturon, metaflumizone, methiocarb and PFOS - perfluorooctanesulfonic acid) from surface water (SW) samples. The primary conditions influencing the efficiency of the SPE, namely the sample pH and volume, the elution and extraction solvent and respective volumes, and the amount of MWCNTs packed in each cartridge, were optimized with the pristine material [1]. The recoveries obtained were above 60% for 5 out of the 8 target pollutants (acetamiprid, atrazine, carbamazepine, diclofenac and isoproturon), when using a low amount of adsorbent (50 mg) and an eco-friendly solvent (ethanol) for both conditioning and elution steps. Moreover, the MWCNT cartridges can be reused for at least 3 consecutive cycles without loss of efficiency and are cheaper than typically employed commercial cartridges. The introduction of oxygenated surface groups on the material, through a controlled HNO_3 hydrothermal oxidation methodology [2], enhanced the recoveries obtained for the industrial compound PFOS and the carbamate pesticide methiocarb (attributed to the hydrogen bond adsorption mechanism), but reduced those observed for the neonicotinoid pesticide acetamiprid and for the pharmaceuticals carbamazepine and diclofenac (suggesting *π-π* dispersive interactions). In the specific case of methiocarb, a good correlation was found between the recovery obtained and the amount of oxygenated surface groups on functionalized MWCNTs (Figure 1), the recovery's increase being mostly ascribed to the increase of phenols, and carbonyl and quinone groups. Therefore, the functionalization method applied to MWCNTs allowed the fine tune of the surface chemistry of the carbon material under study according to the specific micropollutants to be extracted from SW samples. This work offers a new insight for the development of more efficient, low-cost and greener methods for pre-concentration of EU multi-class organic micropollutants in water matrices.

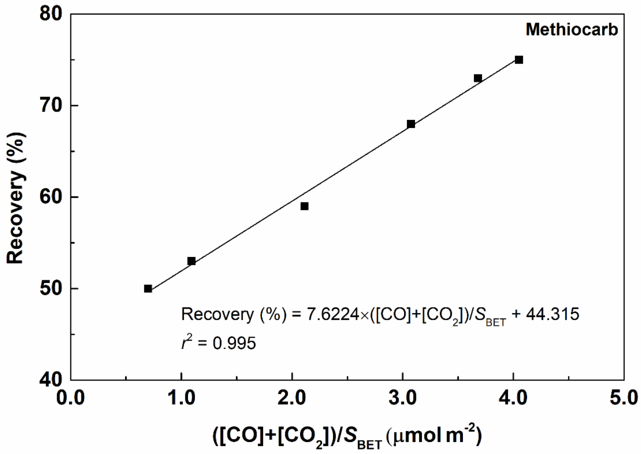

Figure 1. Recovery obtained for methiocarb as a function of ($[CO_2]$ + [CO])/S_{BET}.

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References

[1] M.O. Barbosa, R.S. Ribeiro, A.R. Ribeiro, M.F.R. Pereira, A.M.T. Silva, Solid-phase extraction cartridges with multi-walled carbon nanotubes and effect of the oxygen functionalities on the recovery efficiency of organic micropollutants, Scientific Reports 10 (2020) 22304.

[2] A.M.T. Silva, B.F. Machado, J.L. Figueiredo, J.L. Faria, Controlling the surface chemistry of carbon xerogels using HNO_3-hydrothermal oxidation, Carbon, 47 (2009) 1670-1679.

Sub-Ambient Temperature Sampling of Volatiles from Cheese Uusing Vacuum-Assisted Headspace Thin Film Microextraction and Solid Phase Microextraction

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Keywords: *Cheese, parmesan, solid phase microextraction, thin film microextraction, volatile compound analysis*

Good aroma and flavor are essential quality criteria for cheese commercialization. These two parameters are strongly connected with the volatile fraction produced during the ripening process. In fact, the volatile profile can be considered a fingerprint as it differs according to cheese variety [1].

According to the literature, several studies have been conducted in order to investigate the volatile profile of various hard and semi-hard cheeses, including many well-known varieties such as Emmental, Gruyère, Cheddar, Gouda, Grana and Parmigiano Reggiano and Fossa cheese among others [1]. Recently, the characterization and determination of the volatiles of cheese is carried out using the solid phase microextraction (SPME) coupled with GC, mainly due to its easy operation, high sensitivity, limited risk of artifacts and because of the integration of sampling, extraction, concentration and injection into a single solvent-free step prior to instrumental analysis [1,2].

The objective of this work was to characterize the volatile fraction of Grana Padano parmesan, performing the approaches of headspace solid phase microextraction (HS-SPME) and thin film microextraction (TFME). This cheese is chosen as it is confirmed as one of the most consumed PDO Italian product worldwide.

In this study, we examined the effect of vacuum, temperature and extraction time, in order to improve the extraction efficiency of volatiles in both TFME and HSSPME technique. More specifically, we tested two different extraction temperatures (4 ºC and 50 ºC), three different extraction time (20, 30, 40 min) and the effect of vacuum. By air-evacuating the sample container before or after introducing the sample we expected to accelerate the extraction kinetics of analytes with a low affinity for the headspace [3]. Finally, we compared the efficiency of both methods.

According to our results, via SPME technique only 6 compounds were identified, whereas in the case of TFME 15 compounds were identified. Moreover, it is proved the positive effect of vacuum in both methods. The most surprisingly fact was the effect of vacuum together with 4 ºC, leading to the identification of 7 compounds by the application of TFME. Finally, we deduced that 40 min was the most appropriate extraction time that has a positive impact by the apply of both methods.

Acknowledgements

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References

[1] N. Innocente, M. Munari, M. Biasutti, Characterization by solid-phase microextraction-gas chromatography of the volatile profile of protected designation of origin Montasio cheese during ripening. J. Dairy Sci. 96 (2013) 26-32.

[2] J-H. Lee, R. Diono, G-Y. Kim, D.B. Min, Optimization of solid phase microextraction analysis for the headspace volatile compounds of Parmesan cheese, J Agric Food Chem 51 (2003) 1136–1140.

[3] E. Psillakis, Vacuum-assisted headspace solid-phase microextraction: a tutorial review, Anal. Chim. Acta 986 (2017) 12–24.

Leaching of PAHs and Nicotine from Heat-not-Burn Tobacco Products and Cigarette Butts

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Keywords: *Heat-not-burn tobacco products, Cigarette butts, Leachates, Nicotine, PAHs*

Conventional cigarette butts are the single most collected item in annual international coastal and urban clean-ups. Once dumped, they move through sewer systems and streams into the oceans and/or accumulate in localized areas. Environmental awareness on the disposal of tobacco products mainly focuses on the inability of discarded filters to biodegrade. There is markedly less awareness on the potential of tobacco products to act as point sources and leach toxicants. Indeed, the cumulative effect of many littered cigarette butts may present a significant threat to local organisms as past studies have found cigarette litter toxic to some aquatic species [1]. At the same time, a novel 'heat-not-burn' tobacco products was introduced that is becoming increasingly popular. However, the impact of disposing these heated tobacco sticks and exposing them to environmental water bodies is unknown.

Hitherto, a limited number of published studies attempted to identify and quantify leached organic compounds and all studies focused on conventional cigarette butts. Chemicals belonged to different classes including polycyclic aromatic hydrocarbons (PAHs) [2-4], one alkaloid, several aromatic amines (including nicotine) [5] and carbonyls, three phenols and one terpene were only identified in water leachates produced from smoked CCs.

The complexity of tobacco is expected to result in leachates consisting of highly complex mixtures of compounds and sample preparation is a crucial step for selectively extracting target organic compounds. The present work aims to quantify for the first time, PAHs and nicotine (an emerging organic pollutant) leaching from used and unused tobacco products. HiSorb sorptive extraction is used high capacity PDMS-based probes for the extraction of organic compounds directly from the complex leachates. Results obtained with heated tobacco sticks with aluminum paper (TSAl) were compared to those obtained from conventional cigarettes (CC). Total and bioavailable concentrations of each of the investigated PAHs at both unused and used tobacco products are being determined. As proven, naphthalene is the compound with the highest total and bioavailable concentrations recorded, a fact that might be due to its substantially high water solubility. Used CC displayed the widest range and highest concentrations of PAH compounds detected. The contribution of the different parts of tobacco products (i.e., filter, tobacco and paper) to the amounts of PAHs and nicotine of leachates was assessed for used and unused tobacco products. The results were compared to the dissolved and total concentrations found for tobacco product entities. Tobacco was the major source of metals for both the dissolved and total concentrations. The effects of varying pH, salt and humic acids on the leaching behavior of metals from TPs was also studied, next to the effect of matrix where rainwater, river water and seawater were used to leach metals from used and unused tobacco products. All in all, discarded tobacco products may look like the end point of a life cycle, but there is still a way to go in addressing post-consumer waste clean-up and responsible disposal.

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References

[1] N. Koutela, E. Fernández, ML 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.
[2] H. Moriwaki, S. Kitajima, K. Katahira, Waste on the roadside, "poi-sute" waste: its distribution and elution potential of pollutants into environment., Waste Manag. 29 (2009) 1192-1197.
[3] S. Dobaradaran, TC Schmidt, N. Lorenzo-Parodi, MA Jochmann, I. Nabipour, A. Raeisi, N. Stojanović, M. Mahmoodi, Cigarette butts: An overlooked source of PAHs in the environment?, Environ Pollut. 249 (2019) 932-939.
[4] S. Dobaradaran, TC Schmidt, N. Lorenzo-Parodi, W. Kaziur-Cegla, MA Jochmann, I. Nabipour, HV Lutze, U. Telgheder, Polycyclic aromatic hydrocarbons (PAHs) leachates from cigarette butts into water., Environ. Pollut. 259 (2020) 113916.
[5] S. Alberti, M. Sotiropoulou, E. Fernández, N. Solomou, M. Ferretti, E. Psillakis, UV-254 degradation of nicotine in natural waters and leachates produced from cigarette butts and heat-not-burn tobacco products., Environ Res. (2021) 110695.

Use of Cork By-Products to Determine Fungicides in Water by SPE-GC-MS/MS Methodology

P-54

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Keywords: *Cork by-products, fungicides, gas chromatography- tandem mass spectrometry, solid-phase extraction, sustainable sorbent*

Nowadays, one of the goals of analytical chemistry is the development of green and sustainable sample preparation techniques and analytical methods. Natural cork is a heterogeneous material with a chemical composition mainly formed by hydrophobic biopolymers (lignin and suberin), and hydrophobic polysaccharides (cellulose and hemicellulose), which provide sites for the sorption of organic compounds [1, 2]. Besides, natural cork can be easily thermally treated to enhance the possible interactions with different organic compound. For this reason, this work aims to use this material as a green sorbent for the extraction of fungicides in water by Solid Phase Extraction (SPE).

Fungicides are continuously applied to control the crop production specially in viticulture. This means that these organic compounds are persistent entry in different environment compartments, and residues can easily reach different aquatic ecosystems through the crop soils lixiviation, representing a risk for environmental and human health [3].

The developed analytical methodology was based on solid-phase extraction followed by gas chromatography coupled to tandem mass spectrometry (SPE-GC-MS/MS), employing cork by-products as sorbent to determine 17 fungicides in water samples. To optimize the sampling step, several experimental parameters were studied including sorbent particle size, sorbent amount, and conditioning. A multifactorial experimental design was performed to study the most critical parameters affecting SPE (i.e. type of cork, sample pH, elution solvent). Also, the breackthrough volume and the elution volume were studied. Optimal conditions imply the use of 20 mL of water without pH modification, 50 mg of regranulated cork powder as sorbent, and eluting the retained fungicides with 1 mL of ethyl acetate.

After conducting this optimization, the methodology based on SPE-GC-MS/MS was successfully validated, showing good linearity, repeatability and reproducibility. Quantitative recoveries were evaluated at different concentratioins in a broad range of water matrices including river, fountain, rain and spring. Limits of quantification (LOQs) were at the low ng L^{-1}.

Once the method was validated, it was applied to irrigation water, river water and rain- water samples collected in vineyards areas. Eleven out of the seventeen target fungicides were found in the samples, demonstrating that a partial transfer of the fungicides through runoff water takes place.

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References

[1] G. Mafra, M. T. García-Valverde, J. Millán-Santiago, E. Carasek, R. Lucena, S. Cárdenas. Returning to nature for the design of sorptive phases in solid-phase microextraction, Separations 7 (2020) 2.

[2] A.M.A. Pintor, C.I.A. Ferreira, J.C. Pereira, P.C. Correia, S.P. Silva, V.J.P. Vilar, C.I.M.S. Botelho, R.A.R. Boaventura. Use of cork powder and granules for the adsorption of pollutants: a review, Water. Res. 46 (2012) 3152–3166.

[3] M. Celeiro, L. Vazquez, M. Sergazina, S. Docampo, T. Dagnac, V.J.P. Vilar, M. Llompart, Turning cork by-products into smart and green materials for solid-phase extraction-gas chromatography tandem mass spectrometry analysis of fungicides in water, J. Chromatogr. A 1628 (2020) 461437.

Fabric Phase Sorptive Extraction of Seven Parabens from Human Breast Tissues Prior to High-Performance-Liquid Chromatography – Photodiode Array Analysis of Cancerous and Non-Cancerous Samples

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Keywords: *Bioanalysis, Breast tissue, Fabric phase sorptive extraction (FPSE), Parabens, Sample preparation*

Fabric phase sorptive extraction (FPSE) is a contemporary sophisticated sorbent-based sample preparation technique, pioneered by Kabir and Furton in 2014.[1] FPSE is a highly promising overhaul in the field of sample pretreatment that harmonizes with the principles of Green Analytical Chemistry, contributing to the development of green, cost-effective, fast and efficient methods. The mainstay of the FPSE is the advanced idiosyncrasy of the FPSE extraction medium, resulting from the chemical coating of thin natural or synthetic, cellulose or polyester fabric substrates with sol-gel derived hybrid organic-inorganic polymeric sorbents. The creation of strong covalent bonds, between the permeable fabric and the porous sol-gel polymeric sorbent, is a key factor for the special features of the FPSE device. Therefore, FPSE membranes exhibit high chemical, thermal and solvent stability, increased primary contact surface area, inherent porosity, open geometry and thus great retention capacity and extraction efficiency, leading to fast and direct extraction by both the exhaustive and equilibrium extraction mode. [2]

In this work, FPSE combined with an elaborate homogenization process were the basis for the establishment of a new green simple and economical sample pretreatment workflow for the selective extraction of seven parabens, including methyl paraben (MPB), ethyl paraben (EPB), propyl paraben (PPB), butyl paraben (BPB), isopropyl paraben (iPPB), isobutyl paraben (iBPB), and benzyl paraben (BzPB), from human breast tissue samples and their subsequent determination with a fast high-performance liquid chromatography photodiode-array method. Parabens belong to the wider group of Endocrine Disrupting Chemicals and are widely used as preservatives agents. [3]

The FPSE protocol was meticulously optimized in terms of the type of FPSE membrane, the size of the FPSE membrane, the back-extraction solvent system, the extraction and desorption time, the impact of stirring during both the extraction and elution process. Among nineteen tested FPSE membranes, sol-gel poly(tetrahydrofuran) (sol-gel PTHF) coating on 100% cotton cellulose fabric that represents a medium polarity microextraction device demonstrated the highest extraction efficiency. The chromatographic separation was achieved with a Spherisorb C 18 column and an isocratic mobile phase consisted of 0.05M ammonium acetate and acetonitrile at a flow rate of 1.4 mL/min. The total analysis time was 13.6 min. The developed method was also validated. [4] Limits of detection and limits of quantification ranged from 0.22 to 0.33 and 0.67 to 1.0 ng/g, respectively, for all analytes. Relative recoveries were between 87.6 % and 109.8%, while within-day repeatability and between-day precision RSDs were lower than 10.9% and 11.8%, respectively.

The analytical competence of the developed method was clearly testified by its successful implementation in the bioanalysis of real cancerous and non-cancerous tissue samples emanated from different sub regions of women breasts including axila, the upper left and the right quadrant. In all samples, at least one paraben was detected. Interestingly, concentration levels of parabens in cancerous tissues were higher than in healthy tissues. Results highlighted a bioaccumulation potential of parabens in human breast tissue because of the low-dose long-term exposure of humans, regardless of the statutory limits. Finally, the developed methodology exhibited certain practicality and may be a useful analytical tool for epidemiological and toxicological surveys.

References

[1] A. Kabir, K.G. Furton, Fabric phase sorptive extractors (fpse), US20140274660A1, 2014. https://patents.google.com/patent/US20140274660A1/en .

[2] E. Zilfidou, A. Kabir, K.G. Furton, V. Samanidou, Fabric phase sorptive extraction: current state of the art and future perspectives, Separations 5 (2018) 40.

[3] P.D. Darbre, P.W. Harvey, Paraben esters: review of recent studies of endocrine toxicity, absorption, esterase and human exposure, and discussion of potential human health risks, J Appl Toxicol. 28 (2008) 561–578.

[4] Recommendations from the European Bioanalysis Forum on method establishment for tissue homogenates | Bioanalysis, (n.d.). https://www.future-science. com/doi/full/10.4155/bio.14.34 .

Betaine-based Natural Deep Eutectic Solvents as Promising Green Extraction Agents for Pesticides Determination in Valorized Food By-Products

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Keywords: *by-product, valorization, green chemistry, natural deep eutectic solvent*

Agri-food industry generates a great amount of organic residues that can produce important environmental problems if they are not properly disposed and managed. Adequate recycling of such food waste to obtain energy and other valuable materials has been proposed as a suitable strategy to solve this issue. In this sense, the valorization of food by-products by the extraction of valuable compounds and their transformation in new products intended for livestock feed or food, nutraceutical, and pharmaceutical industries is a widely extended practice that not only has a positive impact on the environment sustainability, but also contributes to decrease production costs and increase the efficiency of the food system [1]. On the other hand, this valorization strategy must consider the possible chemical contaminants or potential pathogens contained in the food by-products to ensure the quality of valorized by-products intended for humans and animal consumption before its use.

However, despite the numerous studies published about food valorization, safety assessment has been rarely carried out. In this sense, the development of new methodologies allowing the reliable evaluation of possible contamination in this kind of food by-products constitutes an issue of utmost importance in the field. Besides, considering sustainability issues, such methodologies should be carried out from a green and environmentally friendly perspective.

Natural deep eutectic solvents (NADESs) have emerged in the last few years as a new generation of extraction solvents accomplishing with the principles and guidelines of Green Chemistry due to their particular characteristics. Those include low toxicity and high biodegradability, easy synthesis, as well as low cost and large availability of raw materials, among others. NADESs are constituted by mixtures of at least two natural substances, a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), with a freezing point much lower than that of either of each component which makes them an interesting alternative to the application of conventional solvents in sample preparation [2]. In this sense, the use of betaine-based NADESs has been widely applied since this natural alkaloid is an excellent HBA, less toxic and cheaper than others commonly used such as choline chloride [3]. However, their application for the extraction of pesticides from food matrices has not been carried out so far.

Thus, in this work we have compared the application of nine NADESs, prepared in our laboratory and constituted by betaine as HBA and different HBDs (i.e. citric, lactic, butanoic and propanoic acids, glycerol, ethylene glycol, propylene glycol, fructose and glucose), for the extraction of pesticides from citrus by-products in order evaluate the occurrence of these contaminants in such matrices and, consequently, to ensure the quality and safety of the products obtained from their valorization. With this aim, a NADES-based liquid-liquid extraction was applied for the recovery of the target compounds followed by gas chromatography-mass spectrometry determination. Results indicated that the combination of betaine with propylene glycol or butanoic acid in molar ratios 1:4 and 1:2, respectively, provided the efficient extraction of the largest number of target pesticides, simultaneously, as well as the highest recovery values. This data points out the application of betaine-based NADESs as suitable green alternative solvents for the extraction of organic contaminants from citrus fruit by-products, offering a reliable and sustainable strategy for food safety assessment of this kind of products intended to be commercialized within the food industry.

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References

[1] A. Nayaka, Brij Bhushan, An overview of the recent trends on the waste valorization techniques for food wastes. J. Environ. Manage., 233 (2019) 352–370.
[2] A. Santana-mayor, R. Rodríguez-Ramos, A.V. Herrera-Herrera, B. Socas-Rodríguez, Deep eutectic solvents. The new generation of green solvents in analytical chemistry, TrAC-Trend. Anal. Chem., 134 (2021) 1161088.
[3] C. Fanali, S. Della Posta, L. Dugo, A. Gentili, L. Mondello, L. De Gara, Choline-chloride and betaine-based deep eutectic solvents for green extraction of nutraceutical compounds from spent coffee ground, J. Pharm. Biomed. Anal.,189, (2020) 113421.

FPSE-HPLC-PDA Method for the Determination of Inflammatory Bowel Disease Treatment Drugs in Whole Blood, Plasma, and Urine

P-57

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Keywords: *biological matrices, Fabric Phase Sorptive Extraction, HPLC-PDA, IBD, whole blood analysis*

The herein poster reports a novel fabric phase sorptive extraction-high performance liquid chromatography-photodiode array detection (FPSE-HPLC-PDA) method for the simultaneous extraction and analysis of ciprofloxacin, sulfasalazine, and cortisone (used in the treatment of inflammatory bowel disease, IBD) in human whole blood, plasma, and urine samples. The chromatographic analysis was carried out using a Luna C18 (250mm×4.6 mm; 5 μm particle size) column in gradient elution, with a total run time of 20 min. The analytical method was optimized and validated in the range 0.05–10 μg/mL for whole blood, 0.25–10 μg/mL for human plasma, and 0.10–10 μg/mL for human urine. Blank human whole blood, plasma, and urine were used as the sample matrix for the method development and validation; while methyl-p-hydroxybenzoate was used as the internal standard (IS). Weighted-matrix matched standard calibration curves showed a good linearity up to a concentration of 10 μg/mL. The intra- and inter-day accuracy values (precision and trueness) were found in the range from −10.9% to 12.3%, and the performances of the validated FPSE-HPLC-PDA were further tested on real IBD patient samples [1].

This is the first FPSE procedure applied simultaneously to whole blood, plasma, and urine samples for the determination of residual IBD drugs, which possess a wide range of polarity (logP values ranging from 2.30 for Ciprofloxacin, to 1.66 for Cortisone, and 2.92 for Sulfasalazine). The new approach exhibits high potential for immediate use as a rapid, robust and green analytical tool for future clinical and pharmaceutical applications.

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References

[1] A. Kabir, K.G. Furton, N. Tinari, L. Grossi, D. Innosa, D. Macerola, A. Tartaglia, V. Di Donato, C. D'Ovidio, M. Locatelli, Fabric Phase Sorptive Extraction-High Performance Liquid Chromatography-Photo Diode Array Detection Method for Simultaneous Monitoring of Three Inflammatory Bowel Disease Treatment Drugs in Whole Blood, Plasma and Urine, J. Chromatogr B 1084 (2018) 53-63.

FPSE-HPLC-PDA Analysis of Seven Paraben Residues in Human Whole Blood, Plasma, and Urine

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Keywords: *biological matrices, Fabric Phase Sorptive Extraction, HPLC-PDA, parabens, whole blood analysis*

Parabens represent alkyl esters of *p*-hydroxybenzoic acid (PHBA), widely used as preservatives and antimicrobial agents in food, pharmaceutical products and cosmetic products. These compounds are easily absorbed in the human body, thus they have been recently classified as endocrine disrupting compounds (EDCs), which is products that interfere with hormone production, release, transport, metabolism or elimination [1]. The use of parabens is currently limited by numerous institutions for which interest is growing in the development of new and increasingly sensitive methods for their determination in environmental, pharmaceutical, cosmetic and health products.

This poster describes an innovative, fast and sensitive method for the simultaneous determination of seven paraben residues including methyl paraben (MPB), ethyl paraben (EPB), propyl paraben (PPB), isopropyl paraben (iPPB), butyl paraben (BPB), isobutyl paraben (iBPB) and benzyl paraben (BzPB) in human whole blood, plasma and urine. The analytes were extracted from the biological matrix by an innovative technique, fabric phase sorptive extraction (FPSE) and subsequently analyzed by high-performance liquid chromatography (HPLC) coupled with photo diode array (PDA) detector [1].

The separation was conducted using a Spherisorb C18 column with methanol and phosphate buffer as mobile phases. The analytical method has been validated according to the International Guidelines through the construction of a calibration curve for each biological matrix and considering precision (intra and inter day), accuracy, selectivity, LOD, LOQ and robustness. Subsequently, the performance of the analytical method was evaluated on real biological samples collected from healthy volunteers.

The proposed method allows the simultaneous analysis of seven paraben residues in three different complex matrices, including whole blood, and therefore it is easily applicable to monitor these substances in different biological sample matrices; furthermore, extraction technique used in this work is fast, easy and in accordance with the new green analytical chemistry (GAC) principles.

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References

[1] A. Tartaglia, A. Kabir, S. Ulusoy, E. Sperandio, S. Piccolantonio, H.I. Ulusoy, K.G. Furton, M. Locatelli, FPSE-HPLC-PDA analysis of seven paraben residues in human whole blood, plasma, and urine, J. Chromatogr. B, 1125 (2019) 1-10.

Assessment of Contaminants in Cereals with Different Degrees of Processing

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Keywords: *Green extraction techniques, Organic contaminants, Food safety*

Nowadays, society is increasingly aware of the importance of consuming high-quality food products and concerned about certain groups of compounds that could be harmful to public health [1]. The Macaronesia Region mades up of Azores, Madeira, Canary Islands and Cape Verde Archipelago, as an outermost region, is an area especially susceptible to food contamination due to external agents coming from products on the international market.

The peculiarities of these regions, with intensive agriculture, less strict regulations or even their incorrect use, make necessary the food safety assessment to guarantee the quality of their food. Regarding the production of cereals in this geographical area, not only raw materials have to be controlled, but also chemicals and other substances must be monitored during storage, conservation, and manufacturing, following the European Food Safety Authority (EFSA) guidelines [2]. In this sense, apart from biological contamination, the evaluation of pesticides is of special concern. That is why, international and national organizations have established specific regulations for these compounds [1].

Therefore, in the present work, an analytical procedure based on QuEChERS method [3] combined with both, ultra-high performance liquid chromatography (UHPLC)-single quadrupole-time of flight (Q-ToF)-mass spectrometry and gas chromatography (GC)-triple quadrupole (QqQ)-tandem mass spectrometry (MS/MS), has been applied for the determination of pesticides in cereals from the Macaronesia Region with different processing degrees. To ensure the veracity of the analytical results, the methodology was validated following the European Commission guidelines (SANTE/12682/2019 guide) [4].

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References

[1] R. Romero-González. Trace gas and dynamic process monitoring by Raman spectroscopy in metal-coated hollow glass fibres, Anal. Methods 7 (2015) 7193-7201.

[2] European Food Safety Authority (EFSA). (March, 2020). (http://www.efsa.europa.eu/en/topics/topic/pesticides)

[3] M. Anastassiades, S.J. Lehotay, D. Štajnbaher, F.J. Schenck, Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and "Dispersive Solid-Phase Extraction" for the Determination of Pesticide Residues in Produce, J AOAC Int. 86 (2003) 412-31.

[4] Analytical quality control and method validation procedures for pesticide residues analysis in food and feed. Document Nº SANTE/12682/2019.

Green Approach to Extraction of Plant Volatiles from Herbal Teas Using Ionic Liquids

P-60

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Keywords: *citral, estragole, herbal tea, HMIM BTI, HPLC*

Herbal teas are widely used as traditional medicines and refreshing beverages. Volatile plant constituents are important for tea aroma and for their beneficial effects, but in some cases, they could be a reason for safety concerns to human health. For example, citral, *i.e.* a mixture of monoterpene isomeric aldehydes geranial and neral, which is present in lemon balm or Eurasian thyme teas, is presumed to have antimicrobial and anti-inflammatory properties, in addition to its pleasant lemon aroma [1]. On the other hand, estragole, a phenylpropanoid compound present in basil, fennel, or anise teas, is considered as potentially toxic and limited daily intakes are recommended [2]. Reliable methods for the determination of plant volatiles in herbal teas are needed for both, elucidation of composition-activity relationships and the assessment of safety of their consumption. The first step in the conventional analysis of volatiles in herbal teas is their isolation from the aqueous solution, and involves the use of techniques such as liquid/liquid extraction with non-polar and often ecologically inappropriate solvents, solid-phase extraction, hydrodistillation. New approaches, including direct GC injection of aqueous solutions, are proposed more recently [3]. However, current methods have limitations.

As green approach, ionic liquids are considered as one of the promising alternatives to organic solvents in the sample prep procedures. In the present work, we tested the extraction efficiency of ionic liquid 1-hexyl-3-methylimidazolium bis(trifluormethylsulfonyl)imide (HMIM BTI) for the extraction of estragole and citral from aqueous medium.

Standard stock solutions of citral or estragole were prepared in absolute ethanol, and subsequently diluted in water to obtain aqueous solutions of different concentrations. HMIM BTI (100 µL) was added in 10 mL of an aqueous solution. The mixture was vortexed (3 min), and then centrifuged (3000 rpm) to facilitate the separation of phases. HMIM BTI extract (50 µL) was diluted with the same volume of methanol and analyzed by reversed-phase HPLC with UV detection (at 280 nm for estragole and 240 nm for citral). Extraction recoveries were determined at two concentration levels for each analyte, and the applicability of the procedure was further tested using real samples, *i.e.* basil tea (1.75 g/100 mL) for estragole and Eurasian thyme tea for citral (2 g/100 mL). The working ranges were selected based on a priori knowledge of expected concentration levels in the real samples and capacity of the detector. The content of estragole in the basil tea was determined by described HMIM BTI extraction procedure and calculated using calibration curve ($y=10117x+41$, $R^2=0.9999$) of standard solutions of estragole in ethanol in the concentration range 0.01-1.00 mg/mL, which corresponded to 0.2-20 µg/mL in the tea sample.

The extraction efficiency of estragole from aqueous solutions using HMIM BTI turned out to be very good, with recoveries above 90%, *i.e.* 92% and 94% at the concentration levels of 0.4 µg/mL and 20.0 µg/mL, respectively. In the analysis of basil infusion, HMIM BTI extraction step enabled detection and determination of estragole content (0.4 µg/mL). In contrast to estragole, although HMIM BTI extraction enabled the detection of citral in the real sample, the recovery values were below acceptable limits (14% and 21% at 0.2 µg/mL and 1.8 µg/mL, respectively). To the best of our knowledge, recovery values for citral and estragole extracted from aqueous solutions were not reported. However, previous investigation of solid-phase extraction of volatiles from rosemary infusion revealed lower recovery rates for several monoterpenes (70-82% for camphor, 1,8-cineole, and borneol) [4] than those obtained for estragole in this study.

The obtained results revealed that HMIM BTI could be a suitable extracting agent for sample preparation step in phytochemical and pharmaceutical analyses of certain compounds. Furthermore, possibilities for designing tailor-made ionic liquids, together with low amounts of both sample and extracting agent that are sufficient for successful extraction, and simple procedure, give new promising green options for the determination of volatiles in herbal infusions.

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References

[1] D. Ganjewala, A.K. Gupta, R. Muhury, An Update on Bioactive Potential of a Monoterpene Aldehyde Citral, J. Biologic. Active Prod. Nat. 2:4 (2012) 186-199.

[2] European Medicines Agency. EMA/HMPC/137212/2005 Rev 1. Public statement on the use of herbal medicinal products containing estragole. London: 24 November 2014.

[3] B. Sgorbini, C. Cagliero, S. Acquadro, A. Marengo, C. Cordero, E. Liberto, C. Bicchi, P. Rubiolo, Evaluation of volatile bioactive secondary metabolites transfer from medicinal and aromatic plants to herbal teas: Comparison of different methods for the determination of transfer rate and human intake, J. Chromatogr. A 1594 (2019) 173-180.

[4] C. Tschiggerl, F. Bucar, Investigation of the volatile fraction of rosemary infusion extracts, Sci. Pharm. 78 (2010) 483-492.

Spinning Cup-Shaped 3D Printed Device for Immunoaffinity Microextraction of Diclofenac in Wastewaters

P-61

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Keywords: *3D printing, Diclofenac, emerging formats, immunoaffinity extraction.*

The determination of contaminants in environmental samples has been challenging in recent years due to restrictive regulations. For this reason, it is increasingly necessary to determine smaller quantities, which translates into the development of new and efficient sample preparation methods with high selectivity and loading capacity. Within sample preparation approaches those based on solid-phase extraction (SPE) and sequels are more suitable to tackle this challenge. However, the selectivity of the conventional SPE materials is limited and their combination with selective materials, such as antibodies is an interesting approach to be explored [1]. These systems are based on the antigen-antibody recognition and binding and, therefore, its combination with SPE materials could offer novel methodologies with high selectivity and loading capacity that might help solving other drawbacks. In this sense, the application of 3D printing to fabricate these devices can offer the perfect match to obtain the desired methodologies. The fabrication of novel 3D printed structures can open new avenues on sample preparation with innovative ideas that have not been explored before. Stereolithography (SLA) technology, which is based on a point-by-point photopolymerization of an acrylate-based resin on a moving support has certain advantages over other 3D printing technologies (viz. higher printer resolution, smoother surfaces, and fast post-processing steps, among others). However, the selectivity of 3D-printed materials is limited and, therefore, their use for direct sample preparation is quite challenging. Despite of this limitation, the surface of the SLA 3D-printed devices can be properly modified to obtain platforms capable of immobilizing selective ligands or even nanomaterials [2]. Therefore, its combination with antibodies is a clever approach that could led to a new niche of novel sample microextraction procedures.

In this work, a 3D-printed portable sample preparation device (3D cup-shaped piece) was designed, printed and covalently modified with a monoclonal antibody [3] for the quantitative extraction of diclofenac in wastewaters (Fig. 1). In order to obtain the most suitable modification route to immobilize the antibody, different reactions paths were tested and the path with the highest extraction efficiency was selected for further studies. Then, the protocol of the immunoaffinity extraction was optimized, including the use of BSA as capping agent and the elution solvent, among others. Analytical figures of merit were evaluated for the proposed method (loading capacity, breakthrough volume, reusability, reproducibility, and limit of detection). Finally, the optimized extraction protocol was applied to two influent wastewaters from Palma de Mallorca (Spain) without filtering.

Fig. 1. Cup-shaped 3D printed device with covalently attached antibody for diclofenac extraction.

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References

[1] A.L. Krall, S.M. Elliott, M.K. Melinda, B.A. Adams, Detecting sulfamethoxazole and carbamazepine in groundwater: Is ELISA a reliable screening tool?, Environ. Pollut., 234 (2018) 420-428.
[2] E.J. Carrasco-Correa, D.J. Cocovi-Solberg, J.M. Herrero-Martínez, E.F. Simó-Alfonso, M. Miró, 3D printed fluidic platform with in-situ covalently immobilized polymer monolithic column for automatic solid-phase extraction, Anal. Chim. Acta, 1111 (2020) 40-48.
[3] M. Huebner, E. Weber, R. Niessner, S. Boujday, D. Knopp, Rapid analysis of diclofenac in freshwater and wastewater by a monoclonal antibody-based highly sensitive ELISA, Anal. Bioanal. Chem., 407 (2015) 8873-8882.

Solvent-Reducing Methods to Quantify Siloxanes in Wastewater and Sludge

P-62

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Keywords: *Activated Sludge, Siloxanes, Wastewater, WWTP*

Over the years, the consumption and production of volatile methylsiloxanes (VMS), have increased. These compounds are widely used in cosmetic and personal care products and are usually detected in increasingly high concentrations in wastewater treatment plants (WWTPs) [1]. These chemicals enter WWTPs through wastewater, suffering further partition according to their chemical properties. While a smaller fraction remains in the treated effluent, the major percentage is incorporated into the sludge line and can end up in biogas, hampering the use of this renewable fuel on cogeneration or other energy-producing processes due to the formation of SiO_2 deposits in the engine parts [2]. Due to their semi-volatile characteristics, the remainder is lost by volatilization, with the possibility of suffering long-range atmospheric transport. One of the aims of Project LANSILOT is to perform a thorough mass balance of VMSs in a WWTP, to better understand these dynamics, and improve VMSs treatments, enhancing the span of the so far few related studies (e.g. [3]). This effort requires several sampling campaigns that cover daily, weekly and seasonal patterns, focusing on sampling wastewater, liquid and solid sludge, air and biogas. The number of samples to handle in quite high, urging for analytical protocols that can be expedite and at the same time more compliant with the "Green Analytical Chemistry" principles that the classic approaches. In this study, methods aiming the quantification of VMSs in wastewater, liquid and solid sludge and passive air samples were optimized. Small sample amounts were used (30 mL, 20 mL, 2.5 g and 10 g of XAD, respectively). Our proposal relies on liquid-liquid (for water and liquid sludge) and solid-liquid (solid sludge and passive air) extractions with low volume of organic solvents followed by different agitation steps (e.g. vortexing, orbital shaking - see Figure 1, ultrasonication and separation funnels) and a final reduction to 1 mL under a gentle nitrogen stream, before chromatographic analysis by GC/MS.

Figure 1. Setup for orbital shaking in liquid sludge LLE method

The proposed methodologies were validated and reached good accuracy and precision performance results, together with low LODs, allowing the establishment of reliable profiles for the presence of VMS in all the matrices in study. Coplete results of the mass balance are being processed and will be available shortly.

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References

[1] C. Rücker, K. Kümmerer, Environmental chemistry of organosiloxanes, Chem. Rev. 115 (2015) 466-524.

[2] I. Bragança, F. Sánchez-Soberón, G.F. Pantuzza, A. Alves, N. Ratola, Impurities in biogas: Analytical strategies, occurrence, effects and removal technologies, Biomass Bioenerg. 143 (2020) 105878.

[3] A.A. Bletsou, A.G. Asimakopoulos, A.S. Stasinakis, N.S. Thomaidis, K. Kannan, Mass loading and fate of linear and cyclic siloxanes in a wastewater treatment plant in Greece, Environ. Sci. Technol. 47 (2013) 1824–1832.

Boronate Affinity Sorbents Based on Thiol-Functionalized Polysiloxane-Polymethacrylate Composite Materials in Syringe Format for Selective Extraction of Glycopeptides

P-63

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Keywords: *Monoliths; gold nanoparticles; poly-3-mercaptopropyl methylsiloxane; composite material; glycopeptides enrichment*

Glycoproteins play an essential role in diverse biological and clinical events, such as inter and intracellular transport, signal transduction, immune response, and molecular recognition [1]. Besides, they have been associated with many diseases, being used as biomarkers and therapeutic targets in clinical diagnostics [1]. However, the low abundance of glycoproteins in biological samples, jointly with the complexity of these matrices, make that the direct identification of these compounds remains challenging. Consequently, a sample treatment is required before proceeding with their determination. Several methods have been described for glycoproteins and glycopeptides enrichment such as lectin affinity chromatography [2], hydrophilic interaction chromatography [3], hydrazide chemistry [4], or boronate affinity chromatography [5]. In particular, boronate-based supports present particular affinity properties towards solutes (*e.g.,* glycopeptides) containing cis-diol groups, where the interaction based on a specific covalent binding can be easily tailored by adjusting the pH of medium. On the other hand, the well-known features of monolithic materials, particularly polymer monoliths (viz. simple and cost-effective fabrication, high stability over a wide pH range, low backpressure and fast separation of macromolecules) [6] combined with boronic ligands, represent an attractive support for sample pretreatment methodologies.

In this work, two novel boronate affinity monolithic materials able to extract glycopeptides within a polypropylene syringe are described and compared. The first material was synthesized from glycidyl methacrylate (GMA)-based monoliths modified with poly-3-mercaptopropyl-methylsiloxane (PMPMS) followed by attachment of 4-vinylphenylboronic acid (VPBA) via thiol-ene click reaction. The second material was prepared by using gold nanoparticle (AuNP)-modified monoliths as substrate followed by subsequent attachment of PMPMS and VPBA. The resulting materials were used as sorbents for solid-phase extraction (SPE) to selectively preconcentrate glycopeptides from horseradish peroxidase (HRP) digests. The material that gave the superior performance was that prepared with AuNPs due to the presence of abundant boronic acid groups, being its practical applicability also examined. The hybrid material exhibited a satisfactory efficiency of glycopeptide enrichment (identifying 24 glycopeptides from a total of 27) in mixture of tryptic digests of HRP and bovine serum albumin (BSA) (1:100, w/w) were tested (or as testing sample). The sorbent shows low sensitivity (0.5 fmol/μL), good adsorption capacity (25 mg g-1) and suitable reusability (over 10 times). Moreover, the hybrid monolith was successfully applied to the selective enrichment of glycopeptides from human serum digests, without any pretreatment, in which 85 glycopeptides were identified by nano-LC-MS/MS, suggesting a great potential for application in glycoproteome field.

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References

[1] M. Nagae, Y. Yamaguchi, Function and 3D structure of the N-glycans on glycoproteins, Int. J. Mol. Sci. 13 (2012) 8398-8429.
[2] Y. Liu, D. Fu, L. Yu, Y. Xiao, X. Peng, X. Liang, Oxidized dextran facilitated synthesis of a silica-based concanavalin a material for lectin affinity enrichment of glycoproteins/glycopeptides, J. Chromatogr. A 1455 (2016) 147-155.
[3] M.H. Selman, M. Hemayatkar, A.M. Deelder, M. Wuhrer, Cotton HILIC SPE microtips for microscale purification and enrichment of glycans and glycopeptides, Anal. Chem. 83 (2011) 2492-2499.
[4] Y. Zhang, M. Kuang, L. Zhang, P. Yang, H. Lu, An accessible protocol for solid-phase extraction of N-linked glycopeptides through reductive amination by amine-functionalized magnetic nanoparticles, Anal. Chem. 85 (2013) 5535-5541.
[5] H. Li, Z. Liu. Recent advances in monolithic column-based boronate-affinity chromatography, TrAC Trends Anal. Chem. 37 (2012) 148-161.
[6] M. Vergara-Barberán, E.J. Carrasco-Correa, M.J. Lerma-García, E.F. Simó-Alfonso, J.M. Herrero-Martínez, Current trends in affinity-based monoliths in microextraction approaches: A review, Anal. Chim. Acta 1084 (2019) 1-20.

Microwave-assisted Saponification and SPE for the Simultaneous or Alternative Analysis of Dialkyl Ketones and Sterols in Fat

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Keywords: *dialkyl ketones (DAK), fat, microwave-assisted saponification, solid-phase extraction, sterols.*

Sterols and, in particular, phytosterols play an important role in the human diet and in verifying the authenticity of the oil products (e.g., to discriminate olive oil from seed oil). The traditional determination of sterols usually involved a first saponification step, followed by liquid-liquid extraction of the unsaponifiable fraction, TLC for isolation of the sterol and final instrumental determination, most often in gas chromatography (GC) after derivatization.

Interesterification is an industrial process used to redistribute the fatty acids among triglycerides changing the physicochemical characteristics of fat (e.g. changing crystallization behaviour and the melting point, improving plasticity). Different from the enzymatic process, the chemical one leads to the formation of dialkyl ketones (DAKs) as by-products. So far, only two papers have dealt with DAKs determination in food [1,2].

Microwave-assisted saponification followed by a lab-made solid-phase extraction (SPE) was optimized for the characterization of either DAK or sterols or both simultaneously. The final instrumental determination was performed by GC-FID for quantification and GC-MS for confirmation purposes. The proposed method showed good recoveries (>80%) and limit of quantification (0.04-0.07 µg/g for the 4 DAK and of 0.07 µg/g for α-cholestanol). Repeatabilities (n=3) were below 15% for DAKs and generally lower than 6% for sterols. Accuracy on the entire sterol profile was confirmed in comparison to the International Olive Council reference method. The method was finally applied to real-world samples before and after chemical interesterification [3].

References

[1] Mariani, C.; Bellan, G, Sul possibile aumento degli alchilesteri negli oli extra vergini di oliva, Riv. Ital. delle Sostanze Grasse, 88 (2011) 172–181.
[2] Santoro, V.; Baiocchi, C.; Dal Bello, F.; Gastaldi, D.; Aigotti, R.; Zorzi, M.; Pellegrino, A.; Forte, E.; Romaniello, F.; Magni, M. Formation of by-products during chemical interesterification of lipids. Detection and characterization of dialkyl ketones by non-aqueous reversed-phase liquid chromatography-high resolution mass spectrometry and gas chromatography-mass spectrometry, J. Chromatogr. A 1581 (2018) 63–70.
[3] S.Mascrez, S. Danthine, G. Purcaro, Foods, 2021 (under revision).

Vacuum-Assisted Headspace SPME Under Sub-Ambient Temperature for the Analysis of Fish Samples

P-65

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Keywords: *Headspace (HS), Solid-phase microextraction (SPME), sub-ambient temperature, Vacuum-assisted HS.*

Vacuum-assisted headspace solid-phase microextraction (Vac-HS-SPME) has been proposed as a valid technique to increase the performance of conventional HS-SPME in particular in terms of kinetics for the semi-volatiles compounds [1]. Although the total amount extracted at the equilibrium does not change when reduced pressure conditions are applied, the overall result from an applicative viewpoint is an increase of extraction yield at shorter extraction time and milder extraction temperature compared to conventional applications, thanks to the improved kinetics. This is particularly beneficial for analysis of food volatiles for a more comprehensive evaluation of the aroma profile and when heating the sample can easily cause artifact formation.

The advantages of using Vac-HS-SPME in food samples have been explored at sub-ambient temperature (i.e., refrigerated temperature) for the analysis of particularly perishable foods, such as raw fish. The use of reduced pressure conditions allowed to efficiently sampling at refrigerated temperature, obtaining results comparable to regular HS-SPME at room temperature.

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References

[1] E. Psillakis, Vacuum-assisted headspace solid-phase microextraction: A tutorial review, *Anal. Chim. Acta, 986 (*2017) 12-24.

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