Institute of Chemistry
University of Silesia in Katowice
Katowice, Poland

The 41st Symposium Chromatographic Methods of Investigating Organic Compounds

A general information about the 41st Symposium with detailed timetable and complete program

June, 19th – 22nd, 2018
Szczyrk, Poland

List of contents

Preface

After the successful 40th Symposium *Chromatographic Methods of Investigating Organic Compounds*, the Organizing Committee of the 41st Symposium is pleased to you invite you to Szczyrk, Poland (June 19th-22nd, 2018), Meta hotel.

Following the long-standing tradition of the 40 preceding meetings, the emphasis will be on the new developments and interesting applications of chromatographic methods in different disciplines of science, including the -omic sciences, pharmacology, medicine, toxicology, forensics, food chemistry, biology, environmental sciences, *etc*. Moreover, we intend to promote and illustrate usefulness of chemometrics in separation science. Within the framework of a discussion panel we will talk about effective methods for teaching chromatography and the related techniques.

In the scientific program of the 41st Symposium 30 lectures and 39 poster presentations have been scheduled. We hope you will find it inspiring and appreciate its interdisciplinary character.

Prof. Michał Daszykowski

on behalf of the Organizing Committee
of the 41st Symposium

Acknowledgements

I would like to acknowledge efforts of those who have significantly contributed to the organization of the 41st Symposium and previous editions as well as to the recognition of the Symposium by local and international scientific community.

All Members of Local and International Scientific Committees are acknowledged for their valuable help and commitment. In particular, I sincerely thank organizers of four core sessions of the 41st Symposium, namely, Dr.Sc. Ivana Stanimirova, Dr.Sc. Piotr Suder, Dr.Sc. Anna Bodzoń-Kułakowska, Dr.Sc. Marek Smoluch, and Dr. Przemysław Mielczarek for the selection of excellent keynote speakers and invited speakers.

Members of the Honorary Committee are acknowledged for their kind support and advise. I am especially grateful to Prof. Teresa Kowalska.

Prof. Łukasz Komsta is acknowledged for his assistance in creating and round-the-clock technical maintaining of our new Symposium website.

I would like to acknowledge support of the Administrative Committee, and especially I am grateful to Dr. Krystyna Jarzembek.

Last, but not the least, I sincerely thank our Sponsors and Institutional Partners for their generous financial help and support. In particular I am grateful to: Rector of the University of Silesia in Katowice - Prof. Andrzej Kowalczyk, Dean of the Faculty of Mathematics, Physics and Chemistry of the University of Silesia in Katowice - Prof. Karol Kołodziej, Head of the Institute of Chemistry of the University of Silesia in Katowice - Prof. Stanisław Kucharski, Toxlab sp. z o.o. represented by Dr. Rafał Celiński, and The Hot Plasma Orchestra for their concert proposal.

Prof. Michał Daszykowski

Honorary Committee

Prof. Teresa Kowalska, Institute of Chemistry, University of Silesia in Katowice, Poland (Editor-in-Chief of *Acta Chromatographica*, Akadémiai Kiadó)

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Prof. Debby Mangelings, Department of Analytical Chemistry, Applied Chemometrics and Molecular Modelling, Vrije Universiteit Brussel, Brussels, Belgium (Editor of *Chromatographia*, Springer)

Prof. Riccardo Leardi, Department of Pharmaceutical and Food Chemistry and Technology, Faculty of Pharmacy, University of Genova, Genova, Italy

Prof. Vladimir Havlicek, Institute of Microbiology, Czech Academy of Sciences, Prague, and Department of Analytical Chemistry, Faculty of Science, Palacký University, Olomouc, Czech Republic

Dr. Joaquim Jaumot, Institute of Environmental Sciences and Water Research, IDAEA, Spanish Research Council (CSIC), Barcelona, Spain

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Dr.Sc. Dariusz Zuba, Institute of Forensic Research, Kraków, Poland

Dr.Sc. Tomasz Puzyn, Laboratory of Environmental Chemometrics, Faculty of Chemistry, University of Gdańsk, Gdańsk, Poland

Dr. Rafał Celiński, Toxlab Sp. z o.o., Katowice, Poland

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Dr. Joanna Orzeł, Institute of Chemistry, University of Silesia in Katowice, Poland

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Dr.Sc. Marek Smoluch, Department of Biochemistry and Neurobiology, Faculty of Materials Engineering and Ceramics, AGH University of Science and Technology, Kraków, Poland

Dr. Anna Drabik, Department of Biochemistry and Neurobiology, Faculty of Materials Engineering and Ceramics, AGH University of Science and Technology, Kraków, Poland

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MSc Paweł Matuszewski, Institute of Chemistry, University of Silesia in Katowice, Poland

MSc Anna Baranik, Institute of Chemistry, University of Silesia in Katowice, Poland

MSc Ewa Łukojko, Institute of Chemistry, University of Silesia in Katowice, Poland

List of invited speakers

Prof. Bezhan Chankvetadze, Institute of Physical and Analytical Chemistry, School of Exact and Natural Sciences, Tbilisi State University, Tbilisi, Georgia, *Recent developments in HPLC separation of enantiomers with polysaccharide-based chiral columns*

Prof. Riccardo Leardi, Dipartimento di Farmacia, Università degli studi di Genova, Genova, Italy, *Optimization of chromatographic methods by experimental design*

Dr. Joaquim Jaumot, Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain, *MCR-based analysis of metabolomic data: from LC-MS to MS imaging*

Prof. Vladimir Havlicek, Institute of Microbiology of the Czech Academy of Sciences, Prague, Czech Republic and Department of Analytical Chemistry, Faculty of Science, Palacký University, Olomouc, Czech Republic, *Bringing mass spectrometry imaging to the masses*

Prof. Teresa Kowalska, Institute of Chemistry, University of Silesia, Katowice, Poland, *Manifold research potential of TLC/HPTLC and hyphenated TLC/HPTLC*

Prof. Michał Markuszewski, Department of Biopharmaceutics and Pharmacodynamics, Medical University of Gdańsk, Gdańsk, Poland, *Analytical methods development and validation towards application to biological and clinical samples in metabolomics*

Prof. Piotr Młynarz, Department of Bioorganic Chemistry, Wroclaw University of Science and Technology, Wroclaw, Poland, *Metabolomics approach to characterization of fungal metabolism of Penicillium genus capable of mineralizing phosphonoacetic acid*

Dr.Sc. Paweł Wiczling, Department of Biopharmaceutics and Pharmacodynamics, Medical University of Gdańsk, Gdańsk, Poland, *Analyzing chromatographic data using Bayesian multilevel modeling*

Dr.Sc. Dariusz Zuba, Institute of Forensic Research, Kraków, Poland, *Chromatographic techniques in forensic toxicology*

Dr. Izabella Surowiec, Computational Life Science Cluster (CLiC), Department of Chemistry, Umeå University, Umeå, Sweden and Acureomics AB, Umeå, Sweden, *Application of chemometrics in the metabolomics pipeline*

Dr. Karolina Jagiełło, Faculty of Chemistry, University of Gdansk, Gdansk, Poland, *Quantitative Structure-Activity Relationship – useful tool to predict the chromatographic characteristics*

Symposium Topical Collection

Participants are invited to submit manuscripts based on their oral or poster presentations for possible publication in CHROMATOGRAPHIA, with the intention of including them in a Topical Collection devoted to the 41st Symposium. Manuscripts will be subject to a regular refereeing procedure. Please consult the journal's homepage for more details.

Manuscripts are to be delivered electronically not later than **December 30th, 2018** via the journal's online submission and reviewing system which is accessible at: http://www.editorialmanager.com/chro

About *Chromatographia* Journal

Chromatographia is a peer-reviewed international journal dedicated to the latest advances in separation sciences. Its goal is to monitor state-of-the-art research and to promote study, research and improvement within its various application areas, including archaeology, biotechnology, clinical, environmental, food, medical, petroleum, pharmaceutical, polymer and biopolymer research, as well as preparative and process-scale applications. The journal focuses on papers that show the scope and power of separation sciences when combined with spectroscopic methods, in particular with mass spectrometry. In addition to exciting new areas in chromatography, such as ultra-high pressure and high-temperature approaches, *Chromatographia* focuses on hyphenated systems that combine several unit operations with chromatography and electro-based separations, especially on the micro- and nanoscale. Integrated biological procedures (e.g., enzymatic, immunological, receptor-based assays) can also be part of the overall analytical process. Developments in separation-related sampling and sampling-preparation approaches, and in particular the combination of these techniques with the above methodologies, are also comprehensively covered.

Chromatographia welcomes submissions that present significant scientific advances in any of these fields. Originality, novelty and scientific potential impact are the key criteria of the Editorial Board for selecting publications appropriate for *Chromatographia*. Submission of papers describing the application of simple methodologies, established methods or techniques to individual compounds, simple mixtures or matrices is discouraged.

Acceptable paper types include Original Articles, Short Communications, Reviews and Letters to the Editor.

Information about workshop

Tuesday, June 19th, 2018, Symposium venue – Meta hotel

Introduction to design of experiments, by Prof. Dr. Riccardo Leardi
Dipartimento di Farmacia, Università degli studi di Genova, Genova, Italy

The main goal of this workshop is to show the participants that Experimental Design is based on the knowledge of the problem much more than on mathematical or statistical formulas. It will be shown that the key of the success of an Experimental Design is the chemical knowledge, and that the writing of the experimental matrices and the statistical computations can be very easily performed by hand. Under these premises, it will be understood that the specific software (very often not even required) is just a tool, not the center of the procedure.

Scope of the workshop: why optimizing OVAT (One Variable At a Time) is wrong; Full Factorial Designs; Plackett-Burman Designs; Central Composite Design, Multicriterion Decision Making

A few words about workshop leader
Prof. Dr. Riccardo Leardi graduated in Pharmaceutical Chemistry and Technology in 1983. Since then he has been working in the section of Analytic Chemistry of the Department of Pharmaceutical and Food Chemistry and Technology of the Faculty of Pharmacy of the University of Genova. His research field is Chemometrics. His interests are mainly devoted to problems related to food, environmental and clinical data, and to experimental design and process optimization.

In the last years his research focused mainly on genetic algorithms and on three-way methods. He developed a software for the application of genetic algorithms in variable selection and, in collaboration, a software for the application of backward interval PLS to remove non-relevant spectral regions.

He is author of about 90 papers and 90 communications in national and international meetings; he has been an invited speaker in 15 international meetings and in several industries and research centers.

Timetable of the workshop
12:00 – 13:00 – accommodation of participants
13:00 – 14:00 – lunch served at the restaurant (Symposium venue)
14:00 – 19:30 – workshop (with a short coffee break)

Overview of the program of the 41st Symposium

Wednesday, June 20th, 2018

- Session 1 (9:00 – 10:45): *Chromatography in bioanalytical and forensic sciences*
- Discussion panel (11:15 – 12:00): *Effective methods for teaching chromatography and the related techniques*
- Business session 1 (12:00 – 13:00)
- Session 2 (14:30 – 16:15): *Imaging techniques*
- Poster session (16:15 – 17:15)
- Session 3 (17:15 – 19:00): *Metabolomics*

Thursday, June 21st, 2018

- Session 4 (9:00 – 10:45): *Chemometrics in separation science (part 1)*
- Session 5 (11:15 – 13:00): *Chemometrics in separation science (part 2)*
- Session 6 (14:30 – 16:30): *Method development*
- Poster session (16:30 – 17:15)
- Session 7 (17:15 – 18:45): *Environmental analysis*
- Business session 2 (18:45 – 19:15)

Social program of the 41st Symposium

Wednesday, June 20th, 2018

- Cookout (19:30 – …)

Thursday, June 21st, 2018

- Dinner (19:30 – 21:00)
- Chill out with Hot Plasma Orchestra (21:00 – 21:45)
  gypsy swing acoustic music

A detailed timetable of the 41st Symposium

(with names of presenting authors)

From	To	Session	Day 1: Wednesday (20.06.2018)	Session	Day 2: Thursday (21.06.2018)	Day 3: Friday (22.06.2018)
09:00	09:15	S1: Chromatography in bioanalytical and forensic sciences	11: D. Zuba	S4: Chemometrics in separation science	41: R. Leardi	Late breakfast
09:15	09:30					
09:30	09:45					
09:45	10:00		12: A. Martyna		42: K. Jagiełło	
10:00	10:15					Summary and closing of the 41st Symposium
10:15	10:30		13: M. Smoluch		43: P. Wiczling	
10:30	10:45		14: E. Makowicz			
10:45	11:15	**Coffee break**				
11:15	11:30	**Effective methods for teaching chromatography and the related techniques**		S5: Chemometrics in separation science	51: J. Jaumot	
11:30	11:45					
11:45	12:00					
12:00	12:15	BS1	B1: M. Gizler		52: I. Surowiec	
12:15	12:30		B2: M. Rybińska-Gacek			
12:30	12:45		Meetings		53: J. Trawiński	
12:45	13:00				54: Ł. Pieszczek	
13:00	14:30	**Lunch time**				
14:30	14:45	S2: Imaging techniques	21: V. Havlicek	S6: Method development	61: B. Chankvetadze	
14:45	15:00					
15:00	15:15				62: T. Kowalska	
15:15	15:30		22: A. Bodzoń-Kułakowska			
15:30	15:45				63: M. Chutkowski	
15:45	16:00		23: P. Suder			
16:00	16:15				64: S. Declerck	
16:15	16:30	**Coffee break and poster session**			65: C. Thomas	
16:30	16:45			**Coffee break and poster session**		
16:45	17:00					
17:00	17:15					
17:15	17:30	S3: Metabolomics	31: M. Markuszewski	S7: Environmental analysis	71: E. Krawczyk	
17:30	17:45					
17:45	18:00		32: P. Młynarz		72: M. Sajdak	
18:00	18:15					
18:15	18:30		33: S. Macioszek		73: A. Puckowski	
18:30	18:45					
18:45	19:00		34: M. Patejko	BS2	B3: J. Grodowski	
19:00	19:15	**Free time**			B4: E. Reszke	
19:15	19:30			**Free time**		
19:30	20:30	**Cookout**		**Dinner**		
21:00	---			**Hot Plasma Orchestra**		

Plenary sessions - list of lectures

(with underlined names of presenting authors)

Wednesday, June 20th, 2018

8:45 – 9:00 **Opening address**

9:00 – 10:45 **Session 1: *Chromatography in bioanalytical and forensic sciences***
Chairpersons: Prof. Teresa Kowalska and Prof. Michał Markuszewski

9:00 – 9:45 D. Zuba, W. Lechowicz, *Chromatographic techniques in forensic toxicology*

9:45 – 10:15 A. Martyna, G. Zadora, D. Ramos, *Comparison of pyrograms for forensic purposes using score-based likelihood ratios*

10:15 – 10:30 K. Labuz, P. Adamowicz, M. Kała, K. Pyrc, E. Reszke, P. Mielczarek, J. Silberring, M. Smoluch, *Detection of legal highs in the urine of methadone-treated patients by LC-FAPA-MS*

10:30 – 10:45 E. Makowicz, I. Jasicka-Misiak, P. Kafarski, *Profiling of volatile fraction of honeys for botanical origin authentication based on the Polish phacelia honeys*

10:45 – 11:15 **Coffee break**

11:15 – 12:00 **Discussion panel: *Effective methods for teaching chromatography and the related techniques***

12:00 – 13:00 **Business session and meetings**

12:00 – 12:15 M. Gizler, Jagiellonian Center of Innovation, Kraków, Poland
SFC – successfully, fast and cheap. Analytical and preparative scale separation of enantiomers of chiral drugs

12:15 – 12:30 M. Rybińska-Gacek, Tusnovics Instruments Sp. z o.o. (Ltd), Kraków, Poland
About reference materials of Chiron

12:30 – 13:00 *Meetings*

13:00 – 14:30 **Lunch time**

14:30 – 16:15 **Session 2: *Imaging techniques***
Chairpersons: Dr.Sc. Marek Smoluch and Dr.Sc. Piotr Młynarz

14:30 – 15:15 V. Havlicek, T. Pluhacek, D. Luptakova, A. Skriba, M. Petrik, B. Ríhova, R. Dobiás, P. Lyskova, O. Benada, J. Novak, *Bringing mass spectrometry imaging to the masses*

15:15 – 15:45 A. Bodzoń-Kułakowska, P. Suder, R. Arena, Ł. Gąsior, G. Ptak, *Different aspects of single cell analysis using MALDI imaging approach*

15:45 – 16:15 A. Bodzoń-Kułakowska, J. Ner-Kluza, P. Suder, *Desorption electrospray: MS imaging complementary technique or waste of time?*

16:15 – 17:15 Poster session

17:15 – 19:00 Session 3: *Metabolomics*
Chairpersons: Prof. Vladimir Havlicek and Dr. Izabela Surowiec

17:15 – 17:45 M.J. Markuszewski, D. Siluk, A. Yumba Mpanga, J. Jacyna, M. Kordalewska, E. Daghir-Wojtkowiak, S. Macioszek, M. Patejko, R. Wawrzyniak, W. Struck-Lewicka, M. Buszewska-Forajta, M. Waszczuk-Jankowska, R. Kaliszan, *Analytical methods development and validation towards application to biological and clinical samples inmetabolomics*

17:45 – 18:15 N. Stosiek, A. Ząbek, P. Młynarz, M. Klimek-Ochab, *Metabolomics approach to characterization of fungal metabolism of Penicillium genus capable of mineralizing phosphonoacetic acid*

18:15 – 18:45 S. Macioszek, R. Wawrzyniak, M. Kordalewska, A. Mika, T. Śledziński, M. Chmielewski, M.J. Markuszewski*, Application of multiplatform metabolomics in understanding chronic kidney disease*

18:45 – 19:00 M. Buszewska-Forajta, M. Patejko, S. Macioszek, D. Sigorski, E. Iżycka-Świeszewska, D. Siluk, M.J. Markuszewski, *Optimization and application of sample preparation procedure for determination of biologically active compounds in formalin-fixed paraffin-embedded tissues (FFPE)*

19:00 – 19:30 Free time

19:30 – … Cookout

Thursday, June 21st, 2018

9:00 – 10:45 **Session 4: *Chemometrics in separation science (part 1)***
Chairpersons: Dr.Sc. Ivana Stanimirova and Dr. Joaquim Jaumot

9:00 – 9:45 R. Leardi, *Optimization of chromatographic methods by experimental design*

9:45 – 10:15 K. Jagiello, M. Gromelski, U. Judycka, J. Błażejowski, T. Puzyn, *Quantitative Structure-Property Relationship approach - useful tool to predict HPLC retention data*

10:15 – 10:45 P. Wiczling, *Analyzing chromatographic data using Bayesian multilevel modeling*

10:45 – 11:15 **Coffee break**

11:15 – 13:00 **Session 5: *Chemometrics in separation science (part 2)***
Chairpersons: Dr.Sc. Ivana Stanimirova and Prof. R. Leardi

11:15 – 12:00 J. Jaumot, *MCR-based analysis of metabolomic data: from LC-MS to MS imaging*

12:00 – 12:30 I. Surowiec, *Application of chemometrics in the metabolomics pipeline*

12:30 – 12:45 J. Trawiński, R. Skibiński, *Photocatalytic properties of the selected metal oxides – a multivariate comparison with the use of HCA*

12:45 – 13:00 Ł. Pieszczek, M. Daszykowski, *TLC identification of inks enhanced with the multiwavelength imaging and multivariate image analysis*

13:00 – 14:30 **Lunch time**

14:30 – 16:30 **Session 6: *Method development***
Chairpersons: Prof. Łukasz Komsta

14:30 – 15:00 B. Chankvetadze, *Recent developments in HPLC separation of enantiomers with polysaccharide-based chiral columns*

15:00 – 15:30 T. Kowalska, M. Sajewicz, *Manifold research potential of TLC/HPTLC and hyphenated TLC/HPTLC*

15:30 – 16:00 M. Chutkowski, K. Kaczmarski, *If and how UHPLC conditions can change the retention process comparing to classical HPLC*

16:00 – 16:15 S. Declerck, Y. Vander Heyden, D. Mangelings, *A tool to evaluate chiral method transfers in supercritical fluid chromatography*

16:15 – 16:30 C.M. Thomas, D.J. Nowakowski, *Application of Py-GC-MS for analysis of thermal decomposition products from algae*

16:30 – 17:15 Poster session

17:15 – 19:15 Session 7: *Environmental analysis*
Chairpersons: Prof. Bezhan Chankvetadze and Dr. Karolina Jagiełło

17:15 – 17:45 W.E. Krawczyk, *Contributions of ion chromatography to the research of global carbon cycle*

17:45 – 18:15 M. Sajdak, R. Muzyka, M. Chrubasik, S. Słodczyk, M. Pogoda, I. Mazurek, *Tools for detection of illegal waste combustion process in central heating furnaces*

18:15 – 18:45 A. Puckowski, Ł. Grabarczyk, A. Białk-Bielińska, P. Stepnowski, *Analytics and ecotoxicology of selected pharmaceuticals in the aquatic environment*

18:45 – 19:15 Business session

18:45 – 19:00 J. Grodowski, INTERTECH POLAND, Warsaw, Poland
New real time pptv level VOC measurement by PTR MS

19:00 – 19:15 E. Reszke, ERTEC, Poland
G. Schroeder, M. Cegłowski, J. Silberring, M. Smoluch
Construction and analytical applications of the ionization sources of FAPA – type energized with high tension electric fields and microwaves

19:30 Dinner

21:00 – … Hot Plasma Orchestra (gypsy swing acoustic music)

Friday, June 22nd, 2018

10:00 – 10:30 Summary and closing of the 41st Symposium

List of lectures

(with underlined names of presenting authors and arranged in alphabetical order)

1) A. Bodzoń-Kułakowska, P. Suder, R. Arena, Ł. Gąsior, G. Ptak, *Different aspects of single cell analysis using MALDI imaging approach*
2) B. Chankvetadze, *Recent developments in HPLC separation of enantiomers with polysaccharide-based chiral columns*
3) M. Chutkowski, K. Kaczmarski, *If and how UHPLC conditions can change the retention process comparing to classical HPLC*
4) S. Declerck, Y. Vander Heyden, D. Mangelings, *A tool to evaluate chiral method transfers in supercritical fluid chromatography*
5) M. Gizler, *SFC – successfully, fast and cheap. Analytical and preparative scale separation of enantiomers of chiral drugs*
6) J. Grodowski, *New real time pptv level VOC measurement by PTR MS*
7) V. Havlicek, T. Pluhacek, D. Luptakova, A. Skriba, M. Petrik, B. Ríhova, R. Dobiás, P. Lyskova, O. Benada, J. Novak, *Bringing mass spectrometry imaging to the masses*
8) K. Jagiełło, M. Gromelski, U. Judycka, J. Błażejowski, T. Puzyn, *Quantitative Structure-Property Relationship approach - useful tool to predict HPLC retention data*
9) J. Jaumot, *MCR-based analysis of metabolomic data: from LC-MS to MS imaging*
10) T. Kowalska, M. Sajewicz, *Manifold research potential of TLC/HPTLC and hyphenated TLC/HPTLC*
11) W.E. Krawczyk, *Contributions of ion chromatography to the research of global carbon cycle*
12) R. Leardi, *Optimization of chromatographic methods by experimental design*
13) S. Macioszek, R. Wawrzyniak, M. Kordalewska, A. Mika, T. Śledziński, M. Chmielewski, M.J. Markuszewski, *Application of multiplatform metabolomics in understanding chronic kidney disease*
14) E. Makowicz, I. Jasicka-Misiak, P. Kafarski, *Profiling of volatile fraction of honeys for botanical origin authentication based on the Polish phacelia honeys*

15) M.J. Markuszewski, D. Siluk, A. Yumba Mpanga, J. Jacyna, M. Kordalewska, E. Daghir-Wojtkowiak, S. Macioszek, M. Patejko, R. Wawrzyniak, W. Struck-Lewicka, M. Buszewska-Forajta, M. Waszczuk-Jankowska, R. Kaliszan, *Analytical methods development and validation towards application to biological and clinical samples in metabolomics*

16) A. Martyna, G. Zadora, D. Ramos, *Comparison of pyrograms for forensic purposes using score-based likelihood ratios*

17) N. Stosiek, A. Ząbek, P. Młynarz, M. Klimek-Ochab, *Metabolomics approach to characterization of fungal metabolism of Penicillium genus capable of mineralizing phosphonoacetic acid*

18) M. Buszewska-Forajta, M. Patejko, S. Macioszek, D. Sigorski, E. Iżycka-Świeszewska, D. Siluk, M.J. Markuszewski, *Optimization and application of sample preparation procedure for determination of biologically active compounds in formalin-fixed paraffin-embedded tissues (FFPE)*

19) Ł. Pieszczek, M. Daszykowski, *TLC identification of inks enhanced with the multiwavelength imaging and multivariate image analysis*

20) A. Puckowski, Ł. Grabarczyk, A. Białk-Bielińska, P. Stepnowski, *Analytics and ecotoxicology of selected pharmaceuticals in the aquatic environment*

21) E. Reszke, G. Schroeder, M. Cegłowski, J. Silberring, M. Smoluch, *Construction and analytical applications of the ionization sources of FAPA – type energized with high tension electric fields and microwaves*

22) M. Rybińska-Gacek, *About reference materials of Chiron*

23) M. Sajdak, R. Muzyka, M. Chrubasik, S. Słodczyk, M. Pogoda, I. Mazurek, *Tools for detection of illegal waste combustion process in central heating furnaces*

24) K. Labuz, P. Adamowicz, M. Kała, K. Pyrc, E. Reszke, P. Mielczarek, J. Silberring, M. Smoluch, *Detection of legal highs in the urine of methadone-treated patients by LC-FAPA-MS*

25) A. Bodzoń-Kułakowska, J. Ner-Kluza, P. Suder, *Desorption electrospray: MS imaging complementary technique or waste of time?*

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28) J. Trawiński, R. Skibiński, *Photocatalytic properties of the selected metal oxides – a multivariate comparison with the use of* HCA

29) P. Wiczling, *Analyzing chromatographic data using Bayesian multilevel modeling*

30) D. Zuba*, W Lechowicz, Chromatographic techniques in forensic toxicology*

Poster session - list of poster presentations (June, 20th and 21st)

(arranged in alphabetical order of names of presenting authors)

1) Baranik, I. Queralt, B. Zawisza, *New carbon nanocomposites based on graphene oxide in adsorption of metal ions*

2) A. Bojke, C. Tkaczuk, P. Stepnowski, M. Gołębiowski, Application of headspace-solid *phase microextraction followed by gas chromatography mass spectrometry to determine volatile compounds produced by insects and entomopathogenic fungi*

3) M. Daszykowski, J. Orzeł, I. Stanimirova, P. Młynarz, D. Prukała, *Evaluating the influence of the UV radiation, temperature and time of storage upon the stability of Solvent Red 19 using the design of experiments approach*

4) Ł. Dąbrowski, *Some aspects of the organic substances identification in cardboard packaging samples by means of GC/MS*

5) A. Drabik, J. Ner-Kluza, P. Mielczarek, J. Silberring, *Studies of aptamer-protein targets using chromatographic approach*

6) A. Gackowska, W. Studziński , *UV filters and their chloroorganic products as the environmental micro-pollutants*

7) Ł. Grabarczyk, A. Białk-Bielińska, E. Mulkiewicz, A. Puckowski, P. Stepnowski, *Assessment of ecotoxicity and stability of selected fluorochinolone pharmaceuticals*

8) A. Jakubus, K. Godlewska, M. Paszkiewicz, P. Stepnowski, *Preliminary evaluation of the application of selected carbon nanotubes as adsorbent for the selective extraction and preconcentration of six β-blockers from environmental water* samples

9) A. Świetlicka, D. Bożek, J. Kozłowska, K. Jarzembek, P. Dybał, V. Kozik, M. Rojkiewicz, J. Jampilek, A. Bąk, *In silico estimation of basic activity-relevant parameters in rational drug design*

10) A. Kamińska, I.E. Głowacka, G. Chwatko, *Determination of lipoic acid and lipoyllysine contents in human urine after oral supplementation of LA*

11) M. Knaś, M. Daszykowski, *TLC separation and identification of amino acids in a mixture - an exercise proposal*

12) M. Knaś, E. Długosz, T. Kowalska, M. Sajewicz, *Chromatographic determination of the volatile and phenolic compounds contained in the Paulownia tomentosa raw material*

13) K. Kocot, M. Kuban, R. Sitko, *Graphene oxide and multi-walled carbon nanotubes modified by β-cyclodextrins as effective adsorbents in micro-solid phase extraction of uranium ions*

14) M. Gawlik, Ł. Komsta, R. Skibiński, *Metabolite profiling of atypical antipsychotic drug - clozapine with the use of human liver microsomes and LC-MS method*

15) M. Leśko, J. Samuelsson, M. Enmark, T. Fornstedt, K. Kaczmarski, *Evaluating the advantage of higher heat conductivity of core-shell diamond stationary phase particle in gradient mode chromatography at very high pressure*

16) M. Libera, A. Waligóra, K. Tyrpień-Golder, A. Woźnica, T. Płociniczak, K. Bednarczyk, *Correlative analysis of anseriformes feathers*

17) E. Łata, A. Fulczyk, T. Kowalska, M. Sajewicz, *Thin-layer chromatographic investigation of decomposition of anthocyanes*

18) E. Łukojko, R. Sitko, E. Talik, A. Gagor, *Adsorptive properties of cellulose fibers coated with chemically modified amorphous silica*

19) J. Margasińska-Olejak, M. Majchrzak, R. Celiński, J. Stojko, *Fatal poisoning of MDMB-CHMICA, 4-CEC and 4-MEAP*

20) M. Marín-García, L. Alcaide, R. Tauler, *Chemometric study of the HPLC-DAD-FLD-MS analysis of Tamoxifen photodegradation process*

21) L. Marynowski, M. Goryl, M. Bucha, J. Smolarek, A. Detman, A. Sikora, A. Chojnacka, B.R.T. Simoneit, *Trehalose, mannitol and arabitol as indicators of fungal metabolism in geological sedimentary rocks*

22) M. Goryl, L. Marynowski, *Bacterially derived hopanes with biological configuration from Ediacaran sedimentary rocks of the East European Craton*

23) P. Matuszewski, I. Stanimirova, *A comparison of several supervised methods for modelling time-course chromatographic data*

24) J. Ner-Kluza, A. Milewska, A. Dąbrowska, P. Mielczarek, K. Pyrc, P. Suder, *Identification of the ZIKA virus protease NS3 targets with nanoLC-MALDI-TOF/TOF*

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27) K. Piechura, P. Mielczarek, *Chromatography in peptide synthesis*

28) K. Purgat, P. Kubalczyk, I. Miszczak, R. Głowacki
Application of single drop microextraction for the determination of homocysteine thiolactone by capillary zone electrophoresis

29) S. Słodczyk, R. Muzyka, M. Chrubasik, M. Pogoda, M. Sajdak, *PAHs analysis as a method for detection of domestic wastes combustion in central heating furnaces*

30) A.W. Sobańska, A. Prokop, S. Król, A. Olkiewicz, E. Brzezińska, *Application of salting-out thin layer chromatography to the separation of selected amino-acids*

31) A. Szopa, M. Klimek-Szczykutowicz, A. Maślanka, H. Ekiert, *Validation of HPLC-DAD method for schisandra lignans estimation and application of the method for Schisandra chinensis cv. Sadova fruit and leaf extracts analysis*

32) M. Toński, J. Wojsławski, A. Białk-Bielińska, P. Stepnowski, *Application of the HPLC technique for the assessment of the hydrolytic stability of carbamazepine and its transformation products*

33) A. Topolewska, P. Stepnowski, Ł.P. Haliński, *Method development for determination of steroidal glycoalkaloids in food using gas chromatography*

34) A.W. Sobańska, K. Wanat, E. Brzezińska, *Application of the simple and easy-to-access chromatographic (RP-18 TLC) and calculated in silico descriptors to predict the Blood-Brain Barrier permeability of a large and structurally diverse set of compounds*

35) J. Wantulok, D. Swoboda, T. Paździorek, M. Szala, J. Nycz, *Synthesis and identification of derivatives of 4,7-dichloro-1,10-phenanhtroline*

36) G. Wejnerowska, K. Belka, *Application of stir bar sorptive extraction to the determination of polycyclic aromatic hydrocarbons in aqueous samples*

37) J. Wojsławski, M. Toński, A. Białk-Bielińska, P. Stepnowski, J. Dołżonek, *The assessment of carbamazepine and 10,11-dihydro-10-hydroxy carbamazepine sorption in soil*

38) P. Ziobrowski, M. Chutkowski, W. Zapała, *Effect of thermal conditions on the retention behavior of selected test substances in a diamond-based core-shell Flare HILIC column*

39) P. Ziobrowski, M. Chutkowski, J. Kamińska, K. Kaczmarski, W. Zapała, *Sorption properties of selected HILIC columns on the example of quercetin, phenol and caffeine as test substances*

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The 41st Symposium Chromatographic Methods of Investigating Organic Compounds

Book of abstracts

June, 19th – 22nd, 2018
Szczyrk, Poland

Lectures

Session 1: ***Chromatography in bioanalytical and forensic sciences***

Chairpersons: Prof. Teresa Kowalska and Prof. Michał Markuszewski

L11 D. Zuba, W Lechowicz
9:00 – 9:45 *Chromatographic techniques in forensic toxicology*

L12 A. Martyna, G. Zadora, D. Ramos
9:45 – 10:15 *Comparison of pyrograms for forensic purposes using score-based likelihood ratios*

L13 K. Labuz, P. Adamowicz, M. Kała, K. Pyrc, E. Reszke, P. Mielczarek, J. Silberring,
10:15 – 10:30 M. Smoluch
Detection of legal highs in the urine of methadone-treated patients by LC-FAPA-MS

L14 E. Makowicz, I. Jasicka-Misiak, P. Kafarski
10:30 – 10:45 *Profiling of volatile fraction of honeys for botanical origin authentication based on the Polish phacelia honeys*

Lecture code **11**

Chromatographic techniques in forensic toxicology

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Abstract

Forensic toxicology is a discipline of forensic science concerned with the study of toxic substances or poisons, of which there are many thousands. Forensic toxicologists are responsible, among others, for examination of bodily fluids and tissue samples collected during autopsies, blood and/or urine samples taken from drivers or intoxicated persons and interpretation of the obtained results. They also perform tests on samples collected by crime scene investigators. Their jobs involve testing for the presence of gases (e.g., hydrogen sulfide or carbon monoxide); ethyl alcohol; illicit drugs (e.g., amphetamines, cannabis products, cocaine, heroin); new psychoactive substances; prescription drugs (e.g., benzodiazines); metals; and other poisons when poisoning or drug overdoses are expected.

The expert opinion of forensic toxicologists are often the background of the court's decision, therefore analytical methods used in the examinations have to assure sufficient quality. Nowadays, different chromatographic techniques are usually the method of choice. The aim of this presentation is to show analytical approaches used in the Department of Forensic Toxicology of the Institute of Forensic Research in Krakow to determine which toxic substances are present in the bodily fluids and tissues, in what concentrations, and the effects of the substances on the body.

Analytical protocols in which gas chromatography is involved include procedures applied for identification and quantitation of carboxyheamoglobin (HbCO), the marker of intoxication by carbon monoxide, as well as ethyl alcohol and other volatile compounds in blood, urine and other biological materials. In some cases, derivatization of an analyte is needed to convert it to less polar and more volatile substance. Most medicines, drugs of abuse and other toxic substances are identified and determined using liquid chromatography coupled with mass spectrometry. High-performance liquid chromatograph with diode-array detector is routinely used for screening of unknown substances, but a hybrid quadrupole time of flight mass spectrometer is more and more often used for this purpose. In turn, liquid chromatograph with triple quadrupole mass spectrometer is the basic tool used in quantitation of these substances.

Other applications of chromatographic techniques include determination of cations and anions, e.g., in cases when a suspect injected an unknown liquid over the victim's face or/and his/her clothes, and analysis of impurities to confirm or deny the authenticity of a product, e.g. spirits or medicines. Food products are also analyzed in order to find foreign chemicals.

Recent challenges in forensic toxicology, such as enormous increase in the number of psychoactive substances available for consumers being isomers and analogues of controlled drugs or analysis of complex matrices, e.g. materials collected from exhumed bodies, will also be discussed.

Lecture code **12**

Comparison of pyrograms for forensic purposes using score-based likelihood ratios

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Abstract

Chromatographic techniques enable recording many parameters characterising the samples of the microtrace size, which is the common issue in the forensic field, e.g. during hit-and-run car accidents. With growing complexity of data there is an increasing compulsion for developing the tools assisting in their interpretation. Typically, the likelihood ratio (LR) models appreciated by the forensic community for assessing the evidential value of physicochemical data are applied. LR (LR=f(E|H1)/f(E|H2), [1]) interprets the data (E) in the light of two contrasting propositions: H1(H2)-compared recovered and control materials come (do not come) from the same source (e.g. suspected car). However, conventional feature-based LR models (using e.g. signal intensities of the chromatographically separated compounds) suffer from the curse of multidimensionality. Their considerable complexity can be reduced in the score-based LR models. In this concept the evidence expressed by the score, computed as a distance between the recovered and control samples characteristics, is evaluated using LR. A score solely based on a distance, without taking into account typicality, may not reflect the differences between similar samples clearly in a highly multidimensional space. Here we show that boosting the between-samples variance (B) whilst minimising the within-samples variance (W) helps distinguish between samples and improves the score-based LR models performance. Instead of computing the distances in the feature space, the authors use the space defined by ANOVA simultaneous component analysis, regularised MANOVA and ANOVA target projection that find directions with the magnified differences between B and W [2].

The concept was successfully illustrated for 22 plastic containers and automotive samples likely to be found on the scene of car accident, examined using Py-GC-MS. They were pyrolysed at a temperature 750°C for 15 s in the stream of carrier gas (helium). Obtained volatile organic compounds were transported via heated interface to GC-MS module, where they were separated and detected [2].

The developed hybrid LR models [2] delivered low levels of false positive and false negative responses and acceptable ECE plots which indicate that the proposed methodology enables for objective evaluation of evidential value of the analysed polymer materials and can be competitive to the ongoing visual inspection of the chromatograms similarity.

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Acknowledgments

The authors wish to thank Prof. Beata Walczak (University of Silesia in Katowice) for her helpful comments and Dr. Rafał Borusiewicz (Institute of Forensic Research in Krakow; IFR) for conducting part of the analyses. The research was funded by the National Science Center (project Preludium 6, no. 2013/11/N/ST4/01547) and IFR projects (VI K/2013-15 and VI K/2015-17).

Lecture code **13**

Detection of legal highs in the urine of methadone-treated patients by LC-FAPA-MS

Krzysztof Labuz[1], Piotr Adamowicz[2], Maria Kała[2], Krzysztof Pyrc[3,4], Edward Reszke[5], Przemyslaw Mielczarek[6], Jerzy Silberring[6], Marek Smoluch[6,*]

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Abstract

Urine tests are commonly accepted methods to control abstinence and adherence to treatment of patients who undergo methadone maintenance treatment (MMT). Depending on various national guidelines and accessibility of techniques, only selected psychoactive substances are tested in urine of MMT patients. In general, they belong to the few groups of compounds; THC, cocaine, amphetamine, opiates, PCP, and benzodiazepines. It is, however well known that patients enrolled in such replacement programs take psychoactive substances that are not routinely detected by the toxicology laboratories at the hospitals to escape unexpected test. Here, we report semiquantitative detection of legal highs taken by MMT patient, using high pressure liquid chromatography coupled to flowing atmospheric pressure afterglow ion source (LC-FAPA-MS). The data were confirmed by quantitative analysis using LC-ESI-MS/MS.

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Lecture code **14**

Profiling of volatile fraction of honeys for botanical origin authentication based on the Polish phacelia honeys

Ewa Makowicz[1,*], Izabela Jasicka-Misiak[1], Paweł Kafarski[2]

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Abstract

Honey is one of the most complex natural food product. It is a mixture of a variety of different chemical classes of compounds. Its chemical composition is very variable and significantly dependent on huge number of varied factors, such as bee species, botanical ang geographical origin, honey processing, age of honey and storage method. Alongside with constantly increasing interest of consumers of natural and healthy food products, growing popularity of bee products is also observed, mostly honeys. In addition to flavor and nutritional values, therapeutic effect in one of the most valuable qualities of honey. In Poland, average production of honey in last eight years reached about 19 thousand tons (according to Institute of Agricultural Economics and Food Economy). Despite such a large production, still the largest contribution, on the domestic market (as well as in European market) have cheaper honeys, which are characterized by poor quality. Additionally, large fraction of honeys available on the Polish market is falsified by addition of glucose – fructose syrups or admixes with imported inferior quality honeys. Therefore, nowadays honey quality and authenticity evaluation is an important applied research area with relevant impact on industry and consumer production. Currently, the widely used traditional method for determination of the botanical origin of honeys is melissopalynology. Despite the fact that this method is characterized by high accuracy and precision, it is not sufficient for a clear assessment of the authenticity of the honey origin. Nowadays, there is a strong growth in number of different methods being proposed as more appropriate for determination of honey quality and origin.

The main purpose of presented study was to isolation and identification of volatiles compounds from Polish rare phacelia honeys. Analyzed honeys samples were from different years (2014 - 2018) and different geographical regions.

During the research three different methods of volatiles extraction were applied (USE, SPE and HS – SPME with PDMS/CAR/DVB fiber. Each extract was analyzed by GC-MS. Based on the obtained results an unique chemical fingerprint was create. Furthermore, for USE and SPE extracts HPTLC method was applied, which allow us to constructing something like code-bars, which were useful for differentiate honeys.

Business session

Lecture code B1

SFC – successfully, fast and cheap. Analytical and preparative scale separation of enantiomers of chiral drugs

Marzena Gizler*
Jagiellonian Center of Innovation, Krakow, Poland
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Abstract
Chiral compounds may present different pharmacological or toxic properties. An example of the consequences of using them as racemates have been thalidomide. The importance of chirality of drugs has been recognized , therefore separation of those compounds may be a very important issure.
Nowodays, the most popular methods separation of enantiomers mixture is HPLC. However, Super fluid chromatography (SFC) may be a faster and cheaper alternative to normal-phase separation by liquid chromatography.
The subject of this presentation is to present SFC as more effective technology which allows significant reduction time and cost of analysis of chiral compounds.
In addition, we will present advantages of transfer an analytical method to preparative scale using to SFC system.

Lecture code B2

About reference materials of Chiron

Małgorzata Rybińska-Gacek*
Tusnovics Instruments Sp. z o.o.
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Abstract
Chiron is an expert in reference materials for over 30 years and we are still leading in this field. Company offers a varied, flexible and innovative range of over 10 000 reference materials, specifically designed and developed to suit the needs of individual customers.
Chiron is well-known for reference materials which are applied in petroleum exploration and oil spill analysis, a large range of alkylated polyaromatic compounds and PAH metabolites, pollutants found in food and the environment, and for the introduction of many new carbon 13-labelled drug standards.
Toxicology is a special range of fast developing where Chrion provides a special offer. Accurate and traceable results are vital for all disciplines to ensure correct identification, the highest standard of treatment, legally defensible prosecution or other important application. Chiron offer a wide range of drug and metabolite standards in powder and solution. In addition to native materials, we also have an impressive range of stable isotopically-labelled internal standards, including a particular focus on carbon 13 labelled materials, considered the 'gold standard' for forensic analysis.
Chiron recognizes that the drug scene is rapidly evolving and we pride ourselves on being quick to react to trends, resulting in us being 'first to market' with many New Psychoactive Substances.

Session 2: ***Imaging techniques***

Chairpersons: Dr.Sc. Marek Smoluch and Dr.Sc. Piotr Młynarz

L21 14:30 – 15:15
V. Havlicek, T. Pluhacek, D. Luptakova, A. Skriba, M. Petrik, B. Ríhova, R. Dobiás, P. Lyskova, O. Benada, J. Novak
Bringing mass spectrometry imaging to the masses

L22 15:15 – 15:45
A. Bodzoń-Kułakowska, P. Suder, R. Arena, Ł. Gąsior, G. Ptak
Different aspects of single cell analysis using MALDI imaging approach

L23 15:45 – 16:15
A. Bodzoń-Kułakowska, J. Ner-Kluza, P. Suder
Desorption electrospray: MS imaging complementary technique or waste of time?

Lecture code **21**

Bringing Mass Spectrometry Imaging to the Masses

Vladimir Havlicek[1,2,*], Tomas Pluhacek[1,2], Dominika Luptakova[1], Anton Skriba[1], Milos Petrik[3], Blanka Ríhova[1], Radim Dobiás[4], Pavlina Lyskova[5], Oldrich Benada[1], Jiri Novak[1]

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Abstract
In this presentation I will show selected clinical mass spectrometry approaches published by our group in 2016-2018 period. These will cover the three aspects: i) *Aspergillus fumigatus* and *Pseudomonas aeruginosa* infections in rats[1] and men: mass spectrometry as specific and sensitive new diagnostic tool. ii) Hypoxic-ischemic encephalopathy in Rice-Vannucci model of rat neonates[2]: towards alternative therapeutic interventions. iii) Intraoperative mass spectrometry[3] on subcutaneous B16/F10 melanomas: from surgery to compound classification. Rapid evaporation ionization mass spectrometry and multimodal imaging will be the dominating tools applied in all three aspects. Special emphasis will be dedicated to elemental and molecular mass spectrometry imaging.

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Acknowledgements
Ministry of Education, Youth and Sports of the Czech Republic (NPU LO1509), Czech Science Foundation (16-20229S).

Lecture code **22**

Different aspects of single cell analysis using MALDI imaging approach

Anna Bodzoń-Kułakowska[1,*], Piotr Suder[1], Roberta Arena[2], Łukasz Gąsior[3], Grażyna Ptak[2,3,4]

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Abstract

Although analytical techniques are improved continuously, the single cell analysis still stays an analytical challenge. Nevertheless, in some studies, this kind of analysis seems to be the only rational approach. The case of reproductive cells analysis – were we have the extremely tiny amount of unique material - is a good example. In our study, we used MALDI mass spectrometry imaging approach to analyze the single oocyte on the ITO glass.

At the beginning, we have tested different MALDI matrixes, and different approaches for matrix application ("dried droplet" approach and covering the sample with the aid of ImagePrep device). The influence of the cell preparation, especially the contamination of the sample with salts appeared to be crucial for obtaining the spectra of good quality. The amount of material presented in the cell turned to be sufficient to perform LIFT analysis and to identify some of the lipids presented in the sample. Using MALDI imaging approach, which means depositing the cells on the transparent ITO glass and marking its position by the marker (nail polish), allows for the fast localization of the cells in the ion source and precise laser targeting. Our way of the measurement makes possible to analyze quite a big amount of oocytes in the reasonable time, which allows obtaining statistically significant results. We hope that our idea of the oocyte analysis help to elucidate chemical changes that accompany different processes in which oocytes are involved. There could be such interesting phenomena as the oocyte maturation, changes in the chemical components during their storage, and much more.

Acknowledgements

This work was supported by the EU Horizon 2020 Research and Innovation Programme (GA no. 692185, Acronym ERAofART), KNOW/IGHZ/RMK/PhD/2016/07 and by the National Science Centre of Poland (GA no. 2016/21/B/NZ3/03631) to GEP.

Lecture code **23**

Desorption electrospray: MS imaging complementary technique or waste of time?

Anna Bodzoń-Kułakowska, Joanna Ner-Kluza, Piotr Suder*

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Abstract

Desorption electrospray is one of the ion sources used in the mass spectrometry based imaging techniques. Although this type of ion source has a set of advantages, like simple, cost effective construction, capability of work in the ambient conditions or compatibility to almost all typically used MS analyzers, some of its disadvantages are difficult to overcome during daily laboratory routine.

Based mainly on our own experiences, we will discuss applicability of this ion source, going through the examples taken directly from the laboratory bench like analyses of brain slides, artificial veins, TLC plates imaging and others. We will try to show the strongest, as well as the weakest sides of analyses using desorption electrospray.

Acknowledgements

The authors would like to thank to the National Science Centre, as this work was supported by the grant number: 2016/21/B/NZ6/01307

Session 3: ***Metabolomics***

Chairpersons: Prof. Vladimir Havlicek and Dr. Izabela Surowiec

L31 17:15 – 17:45
M.J. Markuszewski, D. Siluk, A. Yumba Mpanga, J. Jacyna, M. Kordalewska, E. Daghir-Wojtkowiak, S. Macioszek, M. Patejko, R. Wawrzyniak, W. Struck-Lewicka, M. Buszewska-Forajta, M. Waszczuk-Jankowska, R. Kaliszan
Analytical methods development and validation towards application to biological and clinical samples inmetabolomics

L32 17:45 – 18:15
N. Stosiek, A. Ząbek, P. Młynarz, M. Klimek-Ochab
Metabolomics approach to characterization of fungal metabolism of Penicillium genus capable of mineralizing phosphonoacetic acid

L33 18:15 – 18:45
S. Macioszek, R. Wawrzyniak, M. Kordalewska, A. Mika, T. Śledziński, M. Chmielewski, M.J. Markuszewski
Application of multiplatform metabolomics in understanding chronic kidney disease

L34 18:45 – 19:00
M. Buszewska-Forajta, M. Patejko, S. Macioszek, D. Sigorski, E. Iżycka-Świeszewska, D. Siluk, M.J. Markuszewski
Optimization and application of sample preparation procedure for determination of biologically active compounds in formalin-fixed paraffin-embedded tissues (FFPE)

Lecture code **31**

Analytical methods development and validation towards application to biological and clinical samples in metabolomics

Michał J. Markuszewski*, Danuta Siluk, Arlette Yumba Mpanga, Julia Jacyna, Marta Kordalewska, Emilia Daghir-Wojtkowiak, Szymon Macioszek, Małgorzata Patejko, Renata Wawrzyniak, Wiktoria Struck-Lewicka, Magda Buszewska-Forajta, Małgorzata Waszczuk-Jankowska, Roman Kaliszan

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Abstract

Metabolomics approach was proposed for the assessment of diagnostic importance of a set of metabolites from biological samples derived from patients suffered from urogenital tract cancer (e.g. bladder, prostate, renal cancer). The quantitative determination of previously selected metabolites was carried out using high-performance liquid chromatography coupled with tandem mass spectrometry. The analyses were conducted after the analytical method development and complete method validation according to principles embodied by FDA.

The targeted metabolomics allowed for determination of a set of various metabolites of different physico-chemical properties using RP-HPLC-QQQ/MS [1]. The performed quantitative analyses verified and shortened the proposed list of metabolites that had been chosen from untargeted studies. The statistically significant metabolites ($p<0.05$) were related to different biochemical pathways like RNA degradation, purine metabolism or gut floral metabolism which may be involved in cancer occurrence or progression.

In other approach, multiplatform urinary metabolomics has been implemented in order to scrutinize potential biomarkers of bladder cancer. Urine samples were analyzed with the use of high performance liquid chromatography coupled with time of flight mass spectrometry detection (HPLC-TOF/MS) in RP and HILIC chromatographic systems, gas chromatography hyphenated with triple quadruple mass spectrometry detection (GC-QqQ/MS) in a scan mode, as well as Nuclear Magnetic Resonance (1H NMR).

Both targeted and untargeted metabolomics approach are promising tools in developing diagnostic methods that may be useful in cancer detection.

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Lecture code **32**

Metabolomics approach to characterization of fungal metabolism of *Penicillium* genus capable of mineralizing phosphonoacetic acid.

Natalia Stosiek, Adam Ząbek, Piotr Młynarz*, Magdalena Klimek-Ochab

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Abstract

Organophosphorus xenobiotics have great potential applications, but because of the high stability phosphorus-carbon, their fates in the environment are of interest of many research groups in the world. Among eukaryotic microorganisms, mushrooms have suitable enzymes machinery allowing to use of organophosphorus compounds in their cell metabolism, even in the presence of inorganic phosphate in the culture medium. The best examples are filamentous fungi of the genus *Penicillium*, which are known from their ability to metabolise phosphonoacetic acid (PAA) by an enzyme - acid hydrolase.

The aim of the project was to examine in detail the metabolism of three strains of *Penicillium* fungi, including one reference (museum) and two isolated strains from environment capable to metabolize PAA, which were characterised by different PAA hydrolase activity level. The first isolate exhibited a high level of enzyme activity comparable to the reference strain, while the second isolate showed the enzyme activity at zero level.

As it is known from our experiences, metabolomics approach is very useful in the broadly understood taxonomy of fungi, differentiating microorganism's metabolism between drug-resistant and drug-sensitive strains, discriminating filamentous fungal species and tracking particular biochemical pathways.

By use of LC-MS method the low molecular weight compounds differentiating the cell metabolism processes between fungi grown on the substrate with an inorganic phosphorus source and PAA were found. Additionally, metabolites differentiating metabolism of the isolated strains from reference one were delineated. On this basis, the metabolic differences between the investigated species of *Penicillium* depending on their origin were determined.

Lecture code **33**

Application of multiplatform metabolomics in understanding chronic kidney disease

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Abstract

Chronic kidney disease (CKD) constitutes a gradual loss in kidney function over months or years. CKD represents a major public health issue and the prevalence of the disease is estimated to equal 5-15% of the general population. Metabolomics is used to obtain new insight into pathology of various disorders and can help reveal new hypotheses about possible mechanisms of the disease. Metabolomics searches for disturbances in metabolic profiles, based on the measurement of numerous metabolites produced in the organism. They are heterogeneous compounds with different polarity, volatility, present at a broad range of concentrations. Consequently, a few complementary techniques are required to measure whole metabolome in a biological sample.

In this study, the non-targeted metabolomics approach was applied to evaluate potential metabolic differences between patients with CKD (n=30) and healthy (n=30) group. Patients were suffering stage 3 (n=14) and 4 (n=16) CKD. Liquid chromatography time-of-flight mass spectrometry (LC-TOF-MS) with positive and negative ion electrospray ionisation was utilized to acquire serum metabolic profiles. Moreover, to improve metabolite coverage, serum samples were analysed with triple quadrupole gas chromatography mass spectrometry (GC-QqQ-MS) equipped with electron ionisation (EI) source.

Obtained data were subjected to univariate and multivariate statistical analyses which led to selection of metabolites significantly differentiating CKD patients and healthy controls. Moreover, ANOVA was applied to compare two stages of the disease and healthy controls. In both comparisons, the predominant chemical group was acylcarnitines, measured with LC-MS. However, application of GC-MS enabled to detect other groups of statistically significant metabolites, such as sugars and sugar alcohols, cholesterol and pyruvate. Correlation of metabolites with glomerular filtration rate (GFR) was also checked with the use of Spearman's rank correlation coefficient. Among the most highly correlated compounds were: myo-inositol, sorbitol and decatrienoylcarnitine.

To sum up, we found that serum metabolic fingerprints of CKD patients differ from healthy group. Levels of some endogenous metabolites consequently change with the progression of the disease. Additionally, the study proves the advantage of applying a few complementary techniques in metabolomics research.

Acknowledgements

This study was supported by the National Science Centre, Poland, allocated on the basis of the decision number 2012/07/E/NZ7/0441. Authors would like to thank Shimpol A. M. Borzymowski Company for the opportunity to carry out analysis with the use of their GC-MS 8030TQ System.

Lecture code **34**

Optimization and application of sample preparation procedure for determination of biologically active compounds in formalin-fixed paraffin-embedded tissues (FFPE)

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Abstract

Metabolites are described as small (molecular weight less than 1500 Da) molecules derived from the final processes of metabolism. The impact of their quantitative and qualitative changes on organism is determined by scientific study named metabolomics. The main feature of metabolomics is the ability to implement various types of biological samples, with most common urine, serum and tissues. Tissues, in comparison to urine and serum, could be more informative, but at the same time more challenging for analytical utilization due to their high enzymatic activity. Consequently, the usefulness of formalin-fixed paraffin-embedded (FFPE) tissue in metabolomics gains scientific interest because of its stability and possibility of storage at ambient temperature. However, its application demands a laborious sample preparation procedure.

The main aim of the presented study was the development and optimization of a sample preparation method for metabolite extraction from FFPE tissues for qualitative metabolomic analysis. Sample preparation method consisted of three main steps: deparaffinization (paraffin removal and sample purification), metabolites extraction and derivatization, required due to the fact that determination of metabolites was accomplished with the use of gas chromatography coupled with triple quadrupole mass spectrometry (GC-QqQ-MS 8030, Shimadzu, Japan). Development of sample preparation method included optimization of different parameters such as: type and volume of deparaffinization solvent, solvent used in purification step, number of purification cycles, extraction solvent, and thickness of FFPE tissue specimens.

Optimized sample preparation protocol was applied for untargeted analysis of FFPE prostate cancer (CaP) tissues. Study was based on the analysis of FFPE tissues obtained during the prostatectomy procedure from CaP patients (n=5) and healthy volunteers (n=5). Obtained data underwent preprocessing procedure, including identification, normalization and filtration steps. Identification and confirmation of obtained set of compounds was evaluated by AMDIS program. As a result, metabolites from various chemical groups were detected, including fatty acids, organic acids and amino alcohols. Statistical analysis, based on uni- and multivariate techniques, allowed for selection of 10 metabolites, which significantly discriminated ($p<0.01$) compared groups.

Acknowledgments

Authors would like to thank Shimpol A. M. Borzymowski Company for the opportunity to carry out analysis with the use of their GC-MS 8030TQ System. The work has been supported by the National Centre of Science by the project UMO-2016/21/D/ST4/03730

Session 4: ***Chemometrics in separation science (part 1)***

Chairpersons: Dr.Sc. Ivana Stanimirova and Dr. Joaquim Jaumot

L41 R. Leardi
9:00 – 9:45 *Optimization of chromatographic methods by experimental design*

L42 K. Jagiello, M. Gromelski, U. Judycka, J. Błażejowski, T. Puzyn
9:45 – 10:15 *Quantitative Structure-Property Relationship approach - useful tool to predict HPLC retention data*

L43 P. Wiczling
10:15 – 10:45 *Analyzing chromatographic data using Bayesian multilevel modeling*

Lecture code **41**

Optimization of chromatographic methods by experimental design

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Abstract

During the set up of a new chromatographic method, or when trying to improve the performance of an already existing one, several parameters must be tuned in order to get the best possible performance. The "traditional" approach tries to "optimize" them separately, by keeping all of them constant except one. This approach is not correct and is not the best one, since it does not allow to take into account the interactions among variables.

By following the criteria of experimental design, and therefore by changing all the variables simultaneously, the real optimum can instead be found with a relatively small experimental effort. During the presentation some examples of experimental designs applied to chromatographic methods will be shown, demonstrating the superiority of the multivariate approach compared to the univariate one.

Lecture code **42**

Quantitative Structure-Property Relationship approach - useful tool to predict HPLC retention data

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Abstract

Correlations between the experimentally determined values of various cognitively or usefully important quantities and the structural and/or physicochemical descriptors provide a valuable framework for explaining behaviour of the examined system. Such relationships can be found using modern chemometric methods, such as quantitative property-property relationships (QPPR) modelling. This technique was previously applied to predict the HPLC retention parameters [1-5]. Most of them define correlations between the structural properties and the retention parameters. Thus, they provide quantitative information on the structure property-retention relationships (QPRR). Unfortunately, this approach has a limitation – since the predictions are based on the similarity in chemical structure, the applicability domains of such models are limited only to chemicals structurally similar to these used for developing the models. In our study, we used properties (physicochemical and spectral) as predictors [6], assuming that it does not limit the application of QPRR model to chemicals belonging to the same chemical class. This is especially important in case of pharmaceuticals that form a structurally diversified group of chemicals.

The correlation between the retention parameters of ampholytic, biologically active and/or pharmaceutically relevant, substances (obtained for three non-polar HPLC columns at various compositions of mobile phases and pH regimes) and their physicochemical (calculated/spectral) characteristics were investigated. Developed QPRR models create a useful platform for predicting retention parameters of untested chemicals and, to some extent, gaining pharmaceutically valuable information on the biologically active ampholytic substances based on their properties and the conditions of chromatographic separation.

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Lecture code **43**

Analyzing chromatographic data using Bayesian multilevel modeling

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Abstract

It is relatively easy to collect chromatographic measurements for a large number of analytes, especially using gradient chromatographic methods coupled with mass spectrometry detection. Such data often have hierarchical or clustered structure. For example, analytes with similar hydrophobicity and dissociation constant tend to be more alike in their retention than randomly chosen set of analytes. Multilevel models recognize the existence of such data structures by assigning a model for each parameter with its parameters also estimated from data. In this work, a multilevel model is proposed to describe retention time data obtained from a series of wide linear organic modifier gradients of different gradient duration and different mobile phase pH for a large set of acids and bases. The multilevel model consists of i) the same deterministic equation describing the relationship between retention time and analyte-specific and instrument-specific parameters, ii) covariance relationships relating various physicochemical properties of analyte to chromatographically-specific parameters through QSRR-based equations, and iii) stochastic components of intra-analyte and inter-analyte variability. The model was implemented in the Stan software that provides full Bayesian inference for continuous-variable models through Markov Chain Monte Carlo methods.

References

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Acknowledgements

This project was supported by the National Science Centre, Poland (nr. 2015/18/E/ST4/00449)

Session 5: ***Chemometrics in separation science (part 2)***

Chairpersons: Dr.Sc. Ivana Stanimirova and Prof. R. Leardi

L51 J. Jaumot
11:15 – 12:00 *MCR-based analysis of metabolomic data: from LC-MS to MS imaging*

L52 I. Surowiec
12:00 – 12:30 *Application of chemometrics in the metabolomics pipeline*

L53 J. Trawiński, R. Skibiński
12:30 – 12:45 *Photocatalytic properties of the selected metal oxides – a multivariate comparison with the use of HCA*

L54 Ł. Pieszczek, M. Daszykowski
12:45 – 13:00 *TLC identification of inks enhanced with the multiwavelength imaging and multivariate image analysis*

Lecture code **51**

MCR-based analysis of metabolomic data: from LC-MS to MS imaging

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Abstract

Omics research has encouraged the development of instrumental technologies able to deal with these challenging samples from a wide variety of research areas such as biomedical, nutritional or environmental. In this way, new developments in mass spectrometry (MS) based techniques have allowed the emergence of the metabolomics field. The great advantage of these MS-based workflows is the ability to provide massive amounts of both qualitative and quantitative information which, at the same time, allow for non-targeted studies of these complex biological systems [1]. In addition, this MS-based analysis can be performed using different approaches from direct injection to chromatography-coupled separations and imaging. However, this vast quantity of experimentally generated information requires the application of chemometric data analysis strategies to retrieve this hidden knowledge, especially in the case of non-targeted metabolomic studies [2].

In this work, the most common chemometric tools for the analysis of this different MS datasets are introduced focusing especially in the analysis of chromatographic (LC-MS and LC×LC-MS) and imaging data. A common workflow based on the multivariate curve resolution (MCR) method will be presented dealing with some examples related to the assessment of the effects of environmental stressors to biological model organisms.

References

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Lecture code **52**

Application of chemometrics in the metabolomics pipeline

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Abstract

Availability of large cohorts of samples with related metadata has increased in recent years, providing scientists with extensive and well-described material for studies. At the same time, increased availability of modern high-throughput 'omics' technologies resulted in the potential for generating massive amount of chemical data. These developments place high requirements on study planning, execution, and analysis of data [1,2]. From a practical point of view it means that each experimental step, including selection of relevant samples, their chemical analysis and finally extraction and integration of useful information from the obtained data, have to be optimized and strictly controlled. This cannot be achieved without application of chemometric approaches.

The strategy for performing reliable metabolomics analysis of high number of samples will be presented here. This strategy starts with sample selection and, if needed, subdivision of samples into representative analytical batches with application of multivariate characterization and design of experiment approaches. Chemical analysis of samples is performed according to standard operating protocols using GCMS-TOF and LCMS-QTOF untargeted profiling platforms as well as LCMS-QQQ targeted profiling approaches. Experimental drift in the chromatographic data as well as efficiency of data normalization are evaluated with the Orthogonal Projections to Latent Structures (OPLS®) approach. Data analysis is performed with the multivariate data analysis methods, which allow also for integration of results obtained from different analytical batches/experiments. Multiblock data are analyzed with the OnPLS approach. The presented strategy will be discussed based on several examples from metabolomics and lipidomics analyses of samples from clinical studies of autoimmunological and infectious diseases.

Importance of applying multivariate approaches throughout the whole experimental pipeline will be highlighted, together with the practical experience gained from application of metabolomics as exploratory approach in clinical projects.

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Lecture code **53**

Photocatalytic properties of the selected metal oxides - a multivariate comparison with the use of HCA

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Abstract

Although the environmental photocatalysis is being developed for many years, relationships between the simple metal oxides thus far have not been explored. In this study a multivariate comparison of thirteen nanostructured metal oxides (Bi_2O_3, CeO_2, Co_3O_4, Fe_2O_3, NiO, Pr_6O_{11}, SnO_2, $SrTiO_3$, TiO_2, WO_3, $ZnFe_2O_4$, ZnO and ZrO_2) was performed. Solution containing twenty-six psychotropic pharmaceuticals was used as the test mixture. In order to ensure the influence of the dissolved organic matter, all the experiments were conducted in the real river water. Simulated solar radiation was applied as the most environmentally relevant. The irradiated samples were then analyzed with the use of UPLC-ESI-Q-TOF mass spectrometry. The LC-MS profiles, obtained from the photocatalytic samples after 1 h of irradiation, were then submitted to the hierarchical cluster analysis. The cluster dendrogram, as well as the generated heatmap, enabled visualization of the relationships between the studied oxides.

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Lecture code **54**

TLC identification of inks enhanced with the multiwavelength imaging and multivariate image analysis

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Abstract

The thin-layer chromatography (TLC), being a very versatile and relatively inexpensive separation technique, has many successful applications. It also helps in the separation and identification of different dye components from inks. In this context, the usefulness of TLC has been acknowledged by the police and investigators studying authenticity and forgeries of paper documents. Many articles published has proven that different inks can be recognized using the TLC method [1,2]. Nevertheless, there is still need for the development of new analytical approaches that are suitable for the characterization of complex mixtures and assisting in obtaining more objective, precise and reliable results.

Modern TLC densitometers and the multispectral imaging instruments allow for the recognition of dye spot positions and for the evaluation of their densities. However, their relatively high price limits the use of TLC in small laboratories on a wider scale. Optical elements, interferometers and spectrographs are the most expensive and necessary components of the TLC scanners. Charge-coupled devices used as detectors in multispectral cameras are one of the few inexpensive parts of the scanning appliances and are embedded into almost every mobile phone. Therefore, they can be considered for recording images of the TLC plates [3]. By the selection of different illumination sources (fluorescent and white light) one can obtain multiple images of one TLC plate that potentially reveal complementary information. Acquired images can be further processed as three-modal multispectral data cube, where the first two dimensions represent vertical and horizontal coordinates of pixels and the third dimension is formed by values of the RGB channels of each image recorded at different sources of illumination.

In our study we investigate potential of custom-made chamber with three illumination sources and a mobile phone camera for standardized identification of inks developed on the TLC plates. Multispectral-like data cubes were pre-processed as it is done for the hyperspectral data [4]. The multivariate image analysis (MIA) was applied to the unfolded hypercube data. Reduced multi-spectral images of dye components were treated as instrumental signals and used for comparative analysis. A similar methodology can be applied in forensic laboratory for the exploration or identification of ink origin. We demonstrate the potential of combining TLC, inexpensive method of image acquisition and the multivariate image analysis for extraction of complementary chemical information from chromatographic plates.

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Session 6: ***Method development***

Chairperson: Prof. Łukasz Komsta

L61 B. Chankvetadze
14:30 – 15:00 *Recent developments in HPLC separation of enantiomers with polysaccharide-based chiral columns*

L62 T. Kowalska, M. Sajewicz
15:00 – 15:30 *Manifold research potential of TLC/HPTLC and hyphenated TLC/HPTLC*

L63 M. Chutkowski, K. Kaczmarski
15:30 – 16:00 *If and how UHPLC conditions can change the retention process comparing to classical HPLC*

L64 S. Declerck, Y. Vander Heyden, D. Mangelings
16:00 – 16:15 *A tool to evaluate chiral method transfers in supercritical fluid chromatography*

L65 C.M. Thomas, D.J. Nowakowski
16:15 – 16:30 *Application of Py-GC-MS for analysis of thermal decomposition products from algae*

Lecture code **61**

Recent developments in HPLC separation of enantiomers with polysaccharide-based chiral columns

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Abstract

Polysaccharide derivatives represent one of the most successful group of chiral selectors for separation of enantiomers in liquid-phase separation techniques, such as high-performance liquid chromatography (HPLC) [1], supercritical fluid chromatography (SFC) [2], nano-liquid chromatography (nano-LC) [3] and capillary electrochromatography (CEC) [3]. A chiral stationary phase (CSP) has to meet certain requirements in very competitive environment in order to be widely accepted and applied. The major requirements are universality not only from the viewpoint of coverage of various chiral analytes but also from the viewpoint of applicability in various above mentioned modes and compatibility with various type of mobile phases, stability, robustness, versatility and availability. This presentation summarizes our current attempts in order to implement chemo- and enantio-selectivity in the same CSP, to create stable and robust CSPs by covalent attachment of a chiral selector onto silica [4] and creating CSPs with favorable kinetic properties by using superficially porous silica. In the presentation our strategy for obtaining extremely high separation factor (alfa > 100) in HPLC separation of enantiomers, as well as baseline separation of enantiomers on a few-second timescale will be also demonstrated.

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Lecture code **62**

Manifold research potential of TLC / HPTLC and hyphenated TLC / HPTLC

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Abstract

The subject matter of this presentation is an overview of analytical potential of modern thin-layer chromatography in its standard (TLC) and high-performance (HPTLC) version, and also of their hyphenated modes. Particular attention will be paid to the selected practical tasks, like (i) application of chiral thin-layer chromatography to direct enantioseparations and enantioresolutions; (ii) screening of plant extracts with use of so-called "fingerprints" for rapid assessment of fractions with well pronounced antioxidant potential and hence, with healing properties; (iii) screening of plant extracts with use of so-called "fingerprints" hyphenated with direct microbiological detection (known as direct bioautography), in the search for antibacterial properties of selected fractions, i.e., in the search for natural antibiotics; (iv) screening of plant extracts with use of so-called "fingerprints" hyphenated with direct microbiological detection (also known as direct bioautography), in the search for natural pesticides. An added value of thin-layer chromatography is that it can be off-line coupled with mass spectrometry.

In the case of enantioresolutions of enantiomer pairs, thin-layer chromatography offers considerable flexibility in devising and testing unconventional chiral stationary phases, which otherwise are commercially not available. In this sense, TLC outperforms other chromatographic techniques, which rely exclusively on commercial chiral stationary phases. Fast screening of botanical material with use of TLC / HPTLC in the search for antioxidant and antibacterial extract fractions means a considerable and modern contribution to pharmacognosy and healthcare. Isolation of individual active compounds and determination of their chemical structures can serve as precious inspiration for those engaged in devising fully synthetic medicines. Fast screening of botanical material with use of TLC / HPTLC in the search for natural pesticides is a new direction in creating modern, pro-ecological plant protection strategy based on substances of natural origin.

Lecture code **63**

Sorption properties of selected HILIC columns on the example of quercetin, phenol and caffeine as test substances

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Abstract

Analytical-scale investigations of the retention mechanism are undoubtedly very helpful in processes of method development, however to obtain more reliable picture of the retention process, the adsorption studies in nonlinear (overloaded) conditions are also required. In these studies adsorption isotherms are particularly important. The determination of adsorption isotherms and the following treatment and interpretation of the isotherm data is of the utmost importance for preparative separation systems understanding. The adsorption isotherm comprises essential thermodynamic parameters required for computer simulations (for e.g. process optimization). Besides, the shape of the isotherm and the adequate isotherm model provides information about the retention mechanism in a tested column.

The aim of this study was to recognize the interactions between selected compounds exhibiting different properties using diol- Acclaim Mixed Mode HILIC-1, zwitterionic Knauer Eurospher II HILIC and Purospher Star NH2 columns. The studies were conducted using various methanol – water and acetonitrile – water systems as mobile phases and quercetin, phenol and caffeine as test substances.

The investigations were conducted according to the following approach. First, basing on the determined raw adsorption data classical Scatchard plots were used to make preliminary selection of the adsorption isotherm type. Next, the degree of heterogeneity of the stationary phase was determined by calculation of the adsorption energy distribution (AED) and finally proper adsorption isotherm models were proposed by fitting to the experimental adsorption data assisted by statistical evaluation.

Lecture code **64**

A tool to evaluate chiral method transfers in supercritical fluid chromatography

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Abstract

The separation of chiral drug molecules is very important and necessary during the drug life cycle. High-performance liquid chromatography (HPLC) and supercritical fluid chromatography (SFC) are separation techniques applied, with high success rates, to separate chiral molecules. SFC is rather complementary to HPLC and has become an interesting alternative “green” separation technique, since supercritical carbon dioxide is used as the main component of the mobile phase. An advantage of SFC is the possibility to analyze at increased flow rates without the loss of resolution, which is an important aspect in the context of high throughput and the ‘time is money’ mindset of the industry.

Chiral separations are daily, weekly and monthly performed during the discovery, the early and late development of a drug, respectively. As a result, after a certain time, the initial column on which the separation was developed, may perform unacceptably due to ageing. This requires its replacement. Three possibilities were examined which try to minimize the resolution differences during such transfer: the replacement of the old column by an identical column (same selector) of (I) the same or (II) another manufacturer, or (III) by a column with a different particle size. However, the separation outcome of equivalent columns of different manufactures or between columns with different particle sizes may be different. The transfer of an existing chiral method to a new column could therefore be problematic. Till now, no guidelines or criteria exist to evaluate and handle such transfer problems.

This study attempts defining criteria that can be used as a tool for the method transfer from an ‘old/reference’ to a new ‘equivalent’ chiral column, containing the same chiral selector. In addition, transfers between chiral columns with smaller particles (3 µm instead of 5 µm) are studied. Intermediate (time different) precision experiments of 56 pharmaceuticals, measured with two different mobile phases on four columns, are used to define acceptance limits for a successful transfer in terms of resolution. The results from the intermediate precision experiments allowed determining an acceptable deviation factor on the resolution to consider a transfer successful. The second part of the study focuses on an approach to minimize the efforts for method adaptation when the transfer was not successful. Only small method adaptions, like changing modifier concentration, temperature or back-pressure, usually ensure that an unsuccessful method transfer again becomes successful.

Lecture code **65**

Application of Py-GC-MS for analysis of thermal decomposition products from algae

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Abstract

Analytical pyrolysis involves thermal fragmentation of small quantities of complex compounds at elevated temperature (500-1400 °C) in the presence of an inert gas (helium). Very often this technique is hyphenated to gas chromatography–mass spectrometry for separation and detection of compounds from thermal degradation. Pyrolysis - gas chromatography - mass spectrometry (Py-GC-MS) has been identified as a quick and reproducible technique for screening of biomass materials before further thermal processing. In this study a CDS 5200 series pyroprobe interfaced to a PerkinElmer Clarus 680 gas chromatograph close-coupled with a Clarus 600S mass spectrometer was used for analysis of algal samples pyrolysed at 500 °C. The pyrolysis products were separated in the GC oven with the temperature program of between 45 and 250 °C on a PerkinElmer Elite-1701 GC column, and proposed assignments of the main peaks were made from mass spectra data using the NIST 2005 MS library and from assignments found in the literature. This study presents results from Py-GC-MS experiments on a range of four microalgae species (Nannochloropsis gaditana, Chlorella sorokiniana, Isochrysis galbana and Arthrospira platensis) and five macroalgae species (Himanthalia elongata, Ascophyllum nodosum, Fucus vesiculosus, Fucus serratus - brown macroalgae and Ulva lactuca - green macroalgae)in order to investigate their suitability as sources of feedstock for biofuel production or other value-added products.

Semi-quantitative analysis were performed on the pyrolysis products, Py-GC-MS has shown that the pyrolysis of the microalgae species produces a significant amount of fatty oxygenates. These compounds are the pyrolysis decomposition products associated with the fatty acids and triglycerides present in the microalgae feedstock and include other compounds such as alcohols, ketones, long chain alkanes, carboxylic acids and aldehydes. The analytical pyrolysis revealed major differences between macro and microalgae samples. It was observed that a greater proportion/type of carbohydrate derived products are produced from the macroalgae samples. With all of the brown macroalgae samples producing isomannide from the dehydration of mannitol, the main carbohydrate present in brown macroalgae. Other main products include furan derivatives (also originating from mannitol), furfural that is derived from alginic acid and 5-methylfuran-2-carboxaldehyde that is derived from fucoidan. The protein derived decomposition products of macroalgae pyrolysis are the nitrogen containing compounds comprising analogues of pyrrole, indole, pyrazole and pyridine.

Py-GC-MS has been shown to be effective at making predictions of bio-oil composition produced during thermochemical conversion technologies such as hydrothermal liquefaction. For a comprehensive characterisation of algal feedstock additional complementary techniques were used such as thermogravimetric analysis (TGA), bomb calorimetry and elemental analysis.

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Session 7: ***Environmental analysis***

Chairpersons: Prof. Bezhan Chankvetadze and Dr. Karolina Jagiełło

L71 W.E. Krawczyk
17:15 – 17:45 *Contributions of ion chromatography to the research of global carbon cycle*

L72 M. Sajdak, R. Muzyka, M. Chrubasik, S. Słodczyk, M. Pogoda, I. Mazurek
17:45 – 18:15 *Tools for detection of illegal waste combustion process in central heating furnaces*

L73 A. Puckowski, Ł. Grabarczyk, A. Białk-Bielińska, P. Stepnowski
18:15 – 18:45 *Analytics and ecotoxicology of selected pharmaceuticals in the aquatic environment*

Lecture code **71**

Contributions of ion chromatography to the research of global carbon cycle

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Abstract

The first estimates of chemical denudation, more than two hundred years ago, have shown its rate as a number of oysters in a given river during a year. For a long time polar regions were a white spot on the maps showing results of chemical denudation processes as a lowering of the Earth surface. Only fifty years ago Jean Corbel has chosen a glacier covered basin of Austre Lovenbreen on Svalbard for this research. To estimate chemical denudation rates the volume of water flowing out of the basin of known area and ion concentrations converted into the rock mass dissolved in water have been used. At first bicarbonate was titrated and next total hardness obtained with EDTA titration was used worldwide. For a long time chemical analyses have been exchanged for simpler specific conductivity measurements. The results were total solute loads transported out of a given basin, transformed into mm of rock layer removed during a 1000 year time span.

A new model proposed by Sharp et al.[1] enables the partition of the total dissolved load into crustal, marine and atmospheric components. Ion chromatography is widely used to obtain ion concentrations in water, especially in polar regions where these concentrations are low. Origin of ions is discussed and crustal ion loads are summed up to the total crustal load.

Additional information obtained with the Sharp model includes the amount of carbon dioxide sequestered from the atmosphere during the chemical weathering of carbonate and silicate minerals. This is very important for completing a budget for the global carbon cycle (e.g. [2]). In two glacier covered basins on Svalbard around 2865 kg C km-2 yr-1 was consumed in Bayelva [3] and 5242 kg C km-2 yr-1 in Scottbreen [4] whereas in the small karst catchment Londonelva it was only 1560 kg C km-2 yr-1 [5].

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Lecture code **72**

Tools for detection of illegal waste combustion process in central heating furnaces

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Abstract

Combustion of domestic wastes in central heating furnaces has a negative influence on the environment and human health and is one of the main causes of smog formation. Despite the fact that in became illegal in UE it remained a major cause of air pollution. Its scattered character make it difficult to enforce the law and counteract. A significant change in public attitudes has already been done due to information campaigns. Still we lack reliable analytical methods to detect and confirm illegal activity.

The aim of our research was to create useful, reliable and validated analytical tool which would provide evidence for combustion of domestic wastes. Two methods that had the greatest potential have been chosen: elemental analysis of ash by Inductively Coupled Plasma (ICP) and analysis of organic compounds present in ash samples by gas chromatography (GC-MS).

Data from ICP analysis were subjected to the chemometric analysis in order to determine the statistically important variables. Classifications and regression trees method (C&RT) were then utilized in order to prepare a classification algorithm. In 2017 IChPW took part in Regional Air Protection Program for the Silesia Province "Methodology for detection of illegal combustion and co-combustion of waste in central heating furnaces". As a result a computer program "POP Feniks" based on mentioned algorithm, was developed. It is characterized by 97% accuracy, 88% precision, 100% sensitivity and 96% specificity. Herein we demonstrate that data obtained from GC analysis can further improve presented algorithm and increase its accuracy and precision.

Lecture code **73**

Analytics and ecotoxicology of selected pharmaceuticals in the aquatic environment

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Abstract

The problem of pharmaceutical residues has become one of the leading issues in the fields of environmental chemistry and ecotoxicology in recent years. These substances have been recognized as new emerging pollutants, due to their large scale of use and the fact that they are transported via different routes into the aquatic environment. Pharmaceuticals are designed to elicit a specific biological response at low concentrations on selected organisms. However, they may also cause adverse toxicological effects to other environmentally relevant organisms. Therefore, their presence is one of the greatest threats to the environment and human health [1,2].

Since pharmaceuticals do not occur in natural media as single, isolated substances but together with other compounds, usually of the same family or type - the main purpose of this work was to carry out investigations of a representative group of drugs and their mixtures using an ecotoxicological test battery to characterize their environmental hazards. Furthermore, since a complete view of the exposure and risk posed by these pollutants is impossible to ascertain using only ecotoxicological tests [3] - analytical techniques (High-Performance Liquid Chromatography) were applied in order to investigate the actual exposure concentration and the stability of the compounds used in the experiments.

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Acknowledgments

This work was supported by the Polish National Science Centre (NCN) under grant No. UMO 2015/17/B/NZ8/02481.

Business session

Lecture code B3

New real time pptv level VOC measurement by PTR MS.

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Abstract
New design of IONICON PTR MS spectrometers ensures:

* high sensitivity - LOD <1 pptv,
* time resolution <100 ms,
* measurement without sample preparation,
* full mass range registered by TOF in a fraction of a second.
* does not require a carrier gas,
* linearity > 6 orders of magnitude (ppt ... ppm)
* precursor ions - SRI: H3O +, NO +, O2 +.

Novel atmospheric pressure (API) sample introduction options will be announced.

Lecture code B4

Construction and analytical applications of the ionization sources of FAPA – type energized with high tension electric fields and microwaves.

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Abstract
Selected designs of Flowing Ambient Plasma Afterglow (FAPA) devices will be presented based upon published papers and those being subject of the current research performed in both AGH - Academy in Krakow and UAM – University in Poznan.

Perspectives of future development shall be discussed herewith.

Poster session

Poster number **38**

New carbon nanocomposites based on graphene oxide in adsorption of metal ions

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Abstract

Heavy metal ions are common in environment (water, air, plants). They can be created in environment by a mine, car industry, dye industry or a metallurgical process. On the one hand, metal ions are needed to control biological process (e.g. copper, selenium). On the other hand, accumulation of high concentration of metal ions in a living organisms have caused irreversible damage to respiratory system, digestive system and/or circulatory system (e.g. hexavalent chromium, pentavalent arsenic, lead). According to The United State Environmental Protection Agency (USEPA), the maximum concentration of metal ions in drinking water are regulated [1]. In the consequence, analytical chemistry science has been looking for a new sorbent media in adsorption and removal metal ions with environmental samples.

The aim of the work was synthesised a new carbon nanocomposites based on graphene oxide (GO). GO prepared using Hummers method [2]. The surface of GO was decorated with metal oxides such as: cerium(IV) oxides (GO/CeO2) [3], aluminium oxides (GO/Al2O3) [4] and manganese(IV) oxides (GO/MnO2) [5]. The structure of selected new carbon nanocomposites were investigated by spectroscopy and microscopy techniques.

The synthesised carbon nanocomposites show selective adsorption properties toward anionic like As(V) and Se(IV) and cationic metal species like Cr(III), Cu(II) and Pb(II). The maximum adsorption capacities (qmax) of synthesised carbon nanocomposites calculated by Langmuir models were 5.8-30.0 mg g-1, 43.9-53.9 mg g-1 and 14.0-70.2 mg g-1 on GO/CeO2, GO/Al2O3 and GO/MnO2, respectively.

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Poster number **2**

Application of headspace-solid phase microextraction followed by gas chromatography mass spectrometry to determine volatile compounds produced by insects and entomopathogenic fungi

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Abstract

These days, there is a strong necessity of introducing new method and appliance solutions to laboratories. Those solutions must perform the principles of sustainable development and the green chemistry, as this leads to evolution of the techniques, which reduce or even eliminate use of reagents.

Therefore at the beginning of 90's, Prof. J. Pawliszyn with his research group introduced and developed the solid phase microextraction (SPME) [1]. Nowadays, SPME is widely used in analytical practice and became one of the most popular methods of sample preparation and analysis [2]. Solid phase microextraction is used for isolation and enrichment of volatile compounds, which come from various matrices (e.g. environmental, biological and food samples).

Volatile organic compounds produced by infected insects (fungal infection) might be a source of information which compounds are responsible for insect's defense mechanism. Therefore, the aim of this project was analysis of volatile and semi-volatile compounds produced by *Tenebrio molitor* larvae before and after fungal infection by *Metarhizium flavoviride*. A method of the analysis of volatile compounds was developed using DVB/CAR/PDMS fiber (polydimethylsiloxane/carboxen/divinylbenzene). The extraction time was 60 min, the extraction temperature - 105°C, desorption time - 10 min at 250°C. Next stage was identification of volatile compounds produced by larvae before and after fungal infection. Initial research revealed differences in composition of volatile compounds emitted by infected and non-infected insects.

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Acknowledgements

The project was funded by the National Science Centre (NCN) conferred on the basis of the decision number 2016/21/N/NZ4/03613

Poster number **3**

Evaluating the influence of the UV radiation, temperature and time of storage upon the stability of Solvent Red 19 using the design of experiments approach

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Abstract

In the EU countries, diesel oil is spiked with specific compounds, the so-called fiscal markers, in order to designate purpose of its usage and indicate applied tax level [1]. In Poland, in addition to the invisible marker (Solvent Yellow 124), red dyes, either Solvent Red 19 or 164 are introduced [2] as a mandatory diesel fuel additive. Their presence can be confirmed visually, but their amounts are under strict control and a decreased level most likely indicates illegal attempts of fuel counterfeiting. Both red dyes are considered to be stable compounds over time, but storage conditions may have an impact on their stability which may lead to an undesired color fading.

In our study, we evaluated the influence of (*i*) exposure to a relatively mild UV radiation (UV-A), (*ii*) temperature, and (*iii*) time of storage upon the stability of Solvent Red 19 (SR 19). To describe quantitatively the impact of any factor alone or their combination on the dynamics of color fading the design of experiments approach (DoE) [3] was used. A model solution of SR 19 dissolved in hexan (HPLC grade) was prepared (4.6 $mg \cdot L^{-1}$). During the experiment which was carried out according to the two-level full factorial design with three factors, equal volumes of the model solution were incubated at 6ºC and 30ºC for 31 days and solutions were either exposed to UV-A illumination or not along with the solvent samples. All of the samples were stored in two climatic chambers (MK 240 and KB 240, Binder), enabling temperature control and exposure to the UV-A illumination. Samples that required the UV illumination were placed in quarts flasks, and samples incubated in darkness were placed in glass flasks and carefully foiled with thick aluminum sheets. To score the impact of a factor and factor combinations, the absorbance spectra of samples were measured in the visible spectral range using a UV-VIS spectrophotometer (Thermo Scientific Nicolet Evolution 220 LC) coupled with the Peltier system for measurements at controlled temperature.

The results obtained from DoE confirmed that the effect of the UV-A exposure on the stability of SR 19 is statistically significant indicating the largest loss of color intensity over time. This suggests that the chromophore centers present in the SR 19 structure that give a rise to the red color of the dye, are indeed damaged when samples are exposed to any source of the UV-A radiation for a long period of time.

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Acknowledgement

MD, JO, IS, PM, and DP acknowledge the support of the National Science Centre, Poland (research grant no. 2014/13/B/ST4/05007).

Poster number **4**

Some aspects of the organic substances identification in cardboard packaging samples by means of GC/MS

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Abstract

Cardboard is nowadays very popular material used for packaging. It is due to its low price, ability to biodegradation and recycling. Carton boxes are frequently used for food packaging. In this case they are treated with the substances which allow to protect them from moisture. Paper is often treated with an anti-fungal agents that prevent fungus and mold from growing in the package.

The aim of this work was to elaborate GC/MS conditions and data post-processing methods to achieve screening results in qualitative analysis. Samples taken from cardboard boxes were extracted with dichloromethane (DCM) employing ultrasonic bath. Obtained extract from the extraction (two step process) was collected and evaporated under gentle stream of nitrogen. Residue was reconstituted in a small volume of DCM and analyzed with GC/MS. Two different systems were used: with quadrupole (Q) or ion trap (IT) analyzer. The chromatograms and mass spectra obtained were post - processed using different computer software i.e. native GC/MS programs, AMDIS and OpenChrom [1]. Different options in substance identification procedure were tested (chromatogram deconvolution, background subtraction, implementation of filters etc.) and used to identification unknown substances (for example fatty acids) as well as standards like triphenyl phosphate and other.

Final results were presented and advantages and disadvantages of various mass analyzers and post-processing methods were discussed. The elaborated GC/MS conditions and data post-processing methods can be useful for the routine cardboard test in order to organic substances identification in packaging in case of their further usage in agriculture (as a mulch) or as a feed ingredients [2] etc.

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Poster number **5**

Studies of aptamer-protein targets using chromatographic approach

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Abstract

Aptamers are singly stranded oligonucleotides that possess unique properties to fold into a well-defined 3D structure, by which they specifically bind to various targets, from small molecules, even ions, to whole cells and whole organisms. Their biophysical binding characteristics is similar to this found for antibodies, however they can be chemically modified to improve stability or enable labeling, as they are manufactured by chemical synthesis. Aptamers are selected from a large library of oligonucleotides by a process termed SELEX (Systematic Evolution of Ligands by EXponential enrichment). Aptamers are widely used as tools for different approaches, including diagnostic and therapeutic applications. Identification of aptamer's targets has proven difficult to reveal, because of the less specific nature of a partitioning assays. We present a new analytical approach designed to selectively target proteins bound to aptamers. During studies, we have compared four assay approaches using electrophoretic and chromatographic methods for “fishing-out” aptamer -protein targets, followed by mass spectrometry identification. The use of fluorescent-labeled aptamers for tracking the formation of specific aptamer-target complexes provides the possibility to study putative protein conjugates without the necessity of applying enrichment procedures. Furthermore, changes of the hydrophobic properties of fluorescent-labeled aptamer-protein complexes facilitate their separation by the reversed phase chromatography combined with fluorescence detection, followed by mass spectrometry-based protein identification. These comparative results of several methodological approaches confirmed universal applicability of this method to study aptamer-protein interactions with high sensitivity and specificity.

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Poster number **6**

UV filters and their chloroorganic products as the environmental micro-pollutants

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Abstract

Compounds that act as UV filters are usually added to cosmetics and during bath they are washed away from our skin and get into the water. Their presence was identified in surface waters, in swimming pool waters as well as in wastewater [1]. In the presence of a disinfectant (sodium hypochlorite), they can degrade to form new chloroorganic micro-pollutants [2]. In order to control the quality of water and assess the environmental risks posed by new chloroorganic pollution, it is essential to use relatively fast and accurate methods for their identification. However, the choice of the method is determined largely by properties of the analytes tested. It was proved that the effective method for identification of chloroorganic transformation products of 2-ethylhexyl-4-methoxycinnamate acid (EHMC) and 2-ethylhexyl-4-methoxybenzoic acid (EHPABA), representatives of commonly used UV filters, was gas chromatography coupled with a mass spectrometer detector (GC-MS). By means of GC-MS, chlorinated derivatives of cinnamic acid, chlorophenol and chlorobenzene, among others, were identified in the EHMC reaction products [3]. In the case of EHPABA, these are mono and dichloro derivatives of aminobenzoic acid [4]. The results obtained indicate that the above-mentioned UV filters can be a source of toxic micro-pollutants. According to guidelines of World Health Organization (WHO), chlorophenols and chlorobenzene are toxic substances and they are included into a group of pollutants with a special risk to the environment. Information obtained by GC-MS method about transformation products of the compounds tested allowed us to take further actions in order to check the toxicity of the mixtures of chlorination products of UV filters. The obtained results confirmed the hypothesis that under specific environmental conditions, UV filters can form toxic chloroorganic micro-pollutants.

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Poster number **7**

Assessment of ecotoxicity and stability of selected fluorochinolone pharmaceuticals

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Abstract

Nowadays people emit a lot of different kinds of pollutions to the environment. One of the groups of compounds found in the environment as xenobiotics are pharmaceuticals. Due to the high availability of therapeutic agents the amount of drugs in ecosystems is increasing [1, 2]. This makes it necessary to make an environmental risk assessment for this chemicals. Because of the significant risk of run-off of pharmaceuticals to the water reservoirs the use of aquatic organisms is particularly important. One of the most popular test organisms used in ecotoxicological studies is Lemna minor. There is a lot of literature data on the ecotoxicity of pharmaceuticals on this species, but mostly that studies do not take into account the interaction between chemicals which can increase negative effects of exposure to mixtures of chemicals [3]. It makes it necessary to extend the standard ecotoxicological testing procedure with mixture tests. Another aspect, which is often neglected in standard procedures is the stability of test substances under the ecotoxicological test conditions. Factors necessary for the proper development of test organisms (water, light, etc.) can be destructive for analytes [4]. Decomposition of the analite during the test leads to incorrect results, because obtained toxicity parameters are lower than the real one. This results in an erroneous environmental risk assessment what can be dangerous from the point of view of protection of environment. One of the most effective, and hence one of the most popular methods to assess the stability of the analyte during the test is High-Performance Liquid Chromatography (HPLC). Thanks to the stability studies carried out using the HPLC it is possible to assess the reliability of the obtained results. Moreover, if the obtained results are not satisfactory, the conditions of the ecotoxicological test can be changed based on the obtained results (e.g. from static to recirculation conditions). The aim of this research will be to assess the ecotoxicity of a mixture of fluorochinolone drugs and to assess the stability of analytes during the test. The study will be performed according to the OECD 221 guideline.

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Poster number **8**

Preliminary evaluation of the application of selected carbon nanotubes as adsorbent for the selective extraction and preconcentration of six β-blockers from environmental water samples

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Abstract

Nowadays, β-blockers are most commonly prescribed pharmaceuticals worldwide. As a consequence, these drugs are increasingly detected in the various environmental matrices. Additional problem is the limited metabolism of these compounds in body and the lack of effective methods of their removal from sewage [1]. Therefore, more and more often can be hear opinions about the necessity of monitoring of concentrations of these substances in water. Thus, it is vital, the developing of new methods to the isolation and concentration of β-blockers with use of alternative sorbents. An innovative solution is the use of multi-wall carbon nanotubes as a sorptive material in extraction techniques. Our research concern a dispersive solid phase extraction (dSPE) method combined with liquid chromatography-electrospray ionization- tandem mass spectrometry to simultaneous determination and quantification of six β-blockers (atenolol, nadolol, pindolol, metoprolol, propranolol, acebutolol) in environmental water samples. The proposed method is based on a multi-walled carbon nanotubes as a sorbent, especially because of their remarkable sorption capacity. Crucial parameters of dSPE procedure, which may affect extraction efficiency such as type and quantity of suitable sorbent, pH of sample solution and also composition and volume of elution solvent were optimized. Thus, target analytes were completely adsorbed on multi-walled carbon nanotubes with outer diameter less than 8 nm, in ten minutes. Interestingly, only 10 mg of mentioned sorbent was needed. The analyzed water samples (100 mL) were acidified to pH 6. Analytes retained on CNTs surface were desorbed with use 10 mL of mixture containing ACN : ethyl acetate (1:1) (v/v) + 15% NH_4OH. Under the selected conditions the recovery values were calculated. Additionally, in order to verify the credibility of the method, validation parameters were determined.

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Poster number **9**

In silico estimation of basic activity-relevant parameters in rational drug design

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Abstract

Even vague assessment of a molecular property profile, that is crucial for the compound's bioavailability and hence critical for the prospective drug candidate is possible by a priori calculation of molecular descriptors. The ADMET–tailored properties are essentially estimated, based on the molecular structure, as 'intuitive roadmaps' even before the synthesis of the molecule has been rationalized. Molecular descriptors quantifying drug-like properties (DP) are easily calculated on the basis of molecular formulae, however the reliability of the resulting DP values is still questionable.

Lipophilicity is basically known as a first–rate physicochemical parameter increasingly important in description both the pharmacokinetic (ADMET) and pharmacodynamic aspects of drug–receptor/enzyme interactions which often correlates well with the bioactivity of chemicals. The accurate and efficient measurement of lipophilicity is an important requirement in drug design as the created database can be used for log*P* estimation for millions of hypothetical molecules under design. It is possible that some methods for theoretical calculation of lipophilicity might be more or less suitable for specific/heterogeneous series of compounds analyzed, thus a variety of approaches should be employed in namely *consensus* methodology and subsequently compared with the existing empirical data as well[1]. The poor predictive performance of the software packages for theoretical lipophilicity determination can be partially explained by insufficient coverage of the chemical space by measured compounds – models are as good as the data they are based on. Compared to the great number of compounds for which such data are desirable the current experimental data are notably insufficient.

The primary objective of the current study was to investigate a range of various software log*P* predictors for estimation of the numerical lipophilic values for the ensemble of *N*-alkoxyphenylhydroxynaphthalenecarboxamide derivatives and subsequent crossed-comparison with the experimental parameter. Thus, the empirical lipophilicity (log*k*) was compared with the corresponding log*P* characteristics calculated using alternative methods for deducing the lipophilic features. The mean values of the selected molecular descriptors that average over the chosen calculation methods were subsequently correlated with the log*k* parameter in consensus clog*P*. To scrutinize the (dis)similarities between derivatives PCA procedure was applied to visualize the major differences in the performance of molecules with respect to their lipophilic profile, molecular weight and Ro5 violations.

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Poster number **10**

Determination of lipoic acid and lipoyllysine contents in human urine after oral supplementation of LA

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Abstract

In human cells, lipoic acid (LA) is primarily present in the protein-bound form and plays a central role in oxidative metabolism. This LA form, i.e. lipoyllysine (LLys) is covalently bound via its carboxyl group to the ε-amino group of lysine residues [1, 2].

LA is mainly available as dietary supplement [2]. However, at present there is no information, whether externally administered LA is incorporated into protein bound form [1, 2]. Therefore, we decided to investigate the effect of LA supplementation on LLys and LA content in human urine.

We have developed a fast and reproducible method for determination of LA and LLys in human urine after LA supplementation using ion-pair reversed-phase HPLC technique with UV-Vis detection. We have optimized the reduction and derivatization reaction for the selection of the best conditions for determination of LA and LLys. During method development the following parameters were investigated and optimized: (a) the time, pH and volume of tris(2-carboxyethyl)phosphine in the reducing step; (b) the time and an excess of 1-benzyl-2-chloropyridinium bromide in the derivatization step.

Finally, the presented method was validated for urine samples obtained from healthy donors and urine concentration of LA and LLys was monitored after oral administration of LA.

The calibration curves for LA and LLys were linear in the tested range with correlation coefficients better than 0.99. The precisions, expressed as relative standard deviation value, were within range 0-9.4% and 0-8.2% for LA and LLys, respectively.

In the urine collected at the morning, before swallowing the drug, there was no presence of LA and LLys. The analytical results for urinary LA and LLys were normalized against creatinine. After 1, 2, 3, 4, 5, 6, 7, 8 and 9 weeks of oral ingestion of LA, its concentration and LLys concentration in urine was in the range 0.09-0.56 mmol/mol creatinine for LA and 0.06-0.54 mmol/mol creatinine for LLys.

The developed methodology is the first report for the simultaneous determination of LA and LLys in urine in the form of 2-S-pyridinium derivatives by HPLC with ultraviolet detection. Its advantages are a simple sample preparation procedure and low cost.

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Acknowledgements

This work was supported by grant No 2016/23/N/NZ9/00071 from the National Science Centre, Poland.

Poster number **11**

Chromatographic determination of the volatile and phenolic compounds contained in the *Paulownia tomentosa* raw material

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Abstract

Princess tree (*Paulownia tomentosa* Steud.) from the Paulownia family naturally occurs in China, Taiwan, Cambodia, Laos and Vietnam, and it is cultivated in Europe, North America and Australia. This tree belongs to the Paulownia family (*Paulowniaceae*). Herbal raw material consists of leaves, twigs, flowers and fruits - *Folium, Frondes, Flos et Fructus Paulowniae*, used in traditional Chinese medicine.

Paulownia tomentosa is a rich source of various secondary metabolites, mainly prenylated flavonoids. Currently, about 135 compounds have been isolated from the extracts obtained from various parts of this plant. These include flavonoids, lignans, phenolic glycosides, quinones, terpenoids, glycerides, phenolic acids and the various other compounds. Prenylated flavonoids from *Paulownia tomentosa* show a promising pharmacological activity - antibacterial activity against several pathogenic bacterial strains, anti-inflammatory, cytotoxic, and antioxidant activity[1-3]. The results of research on anticancer properties of *Paulownia* have been published. The research is conducted on the influence of the *Paulownia tomentosa* derived active compounds in neurodegenerative disorders, in particular in Parkinson's disease, Alzheimer's disease, epilepsy, cystic stroke and ischemic stroke [4].

The main purpose of this study is qualitative asessment of the volatile and phenolic fraction contained in the *Paulownia tomentosa* raw material. The plant test sample was macerated and subjected to exhaustive extraction in the Soxhlet apparatus. The prepared herbal extract was subjected to a multistage extraction which allowed isolation of individual fractions of phenolic compounds. Each fraction was then analyzed by means of thin-layer chromatography (TLC). The plant sample was also subjected to hydrodistillation according to the standard procedure described in Polish Pharmacopoeia, and essential oil obtained in that way was analyzed by means of gas chromatography coupled with mass spectrometric detection (GC/MS). As a result of the performed analyzes, the TLC fingerprints were obtained for six fractions containing phenolic compounds (including flavonoid aglycones, phenolic acids and flavonoid glycosides) and the composition of the volatile fraction separated from the tested plant was determined and compared to the data on the components contained in *Paulownia tomentosa*, reported in the literature.

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Poster number **12**

TLC separation and identification of amino acids in a mixture - an exercise proposal

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Abstract

Among different courses offered to students of the MSc chemistry program, teaching of chromatography and related techniques has a special place. The 'chromatography' module includes lectures and seminar extended with laboratory exercises. Within the scope of laboratory exercises practical aspects of separation are discussed including suitable methods of sample preparation, the quantitative and qualitative analysis using different chromatographic techniques. Among various chromatographic techniques, the thin-layer chromatography (TLC) is mostly valued for its simplicity, the possibility to handle simultaneous analysis of several samples during a single run, the possibility to perform separation on different stationary phases as well as either in one- or two-mode development variant (allowing to increase resolution by taking an advantage of orthogonal separations) and for large number of ready-to-use qualitative and quantitative methods. Therefore, in our chromatography course practical laboratory training starts with the TLC technique being considered as the basic one.

The subject of the proposed exercise for the MSc students involves the use of TLC to handle the identification of amino acids present in an unknown mixture. Students perform the qualitative TLC analysis using prepared standard solutions of a few aminoacids in order to get familiar with the technique and its specific requirements. In particular, they gain a number of practical skills related with: (i) pre-conditioning of chromatographic plates properly, (ii) the use of glass capillaries and automatic sample applicator, and (iii) the use of advanced multiwavelength densitometer. Moreover, exercise is designed to illustrate how certain effects such as the selection of stationary phase and the selection of a mobile phase and its composition can influence the retention process.

Students improve their knowledge of the TLC technique and learn its principles, they study physicochemical fundamentals of the chromatographic process, get familiar with the separation mechanism as well as with different types of stationary and mobile phases used in TLC, and methods of visualization. In general, they gain practical experience in performing the TLC-based separation and improve their manual skills required in analytical laboratory. In addition, students are encouraged to assess the TLC technique using 'green analytical methods' criteria. Moreover, prior to exercise students have to get familiar with material safety data sheets and are instructed how to handle properly waste chemicals.

Each student hand in to a supervisor a written report. It is an important element of the training and a subject of a careful evaluation according to a certain number of criteria. In general, the report helps students in structuring and embedding acquired knowledge. Moreover, written report, being a compulsory component of exercise, stimulate further development of critical thinking, assists in developing ability of proper and concise presentation and discussion of obtained results, strengthen ability of students to formulate conclusions strictly based on analytical results and related observations (evidence-based learning) and actively stimulate students to polish their writing style.

Poster number **13**

Graphene oxide and multi-walled carbon nanotubes modified by β-cyclodextrins as effective adsorbents in micro-solid phase extraction of uranium ions

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Abstract

An unique magnetic and spectroscopic properties of f-elements contributed to the widespread use of those elements in different industrial fields, including medicine, pharmacy, electronics, metallurgy and nuclear energy. An increasing number of lanthanides and actinides applications in industrial and agricultural fields justify the need for the development of precise, rapid and accurate procedures for their determination [1]. Nevertheless, very low concentrations of lanthanides and actinides in the environment (in the ppb level) and similarities in the physical and chemical properties of those elements make their direct determination very difficult. Various interferences and coincidences emerge especially when it comes to determination of one particular element in the mixture of f-elements. The determination problem grows also when lanthanides and actinides have to be separated from each other.

Among all spectroscopic techniques applied for the determination of f-elements ICP-MS has become the most popular one [2]. Several reasons have contributed to this fact, i.e. short detection time, high accuracy, multielement analysis capability or large dynamic linear range. Despite the widespread use of ICP-MS technique, some disadvantages associated with spectral interferences of the oxides of lower mass analytes with higher ones are inevitable. Since concentrations of actinides in the environment are usually in the ppb range, so often below the instrumental detection limits, application of an appropriate preconcentration/separation step before the actual measurement is necessary.

The aim of this study was to develop precise, rapid and accurate analytical procedures based on dispersive micro-solid phase extraction (DMSPE) with graphene and multi-walled carbon nanotubes functionalized with β-cyclodextrins for the preconcentration of uranium ions by ICP-OES and X-ray fluorescence (XRF) as detection techniques. The obtained nanomaterials were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. In the series of batch experiments the sorption of U ions was examined. Each of the synthesized adsorbent was added to the sample containing U solution and then stirred. In the next step the solution was passed through a cellulose filter using a filtration assembly. Subsequently, the concentration of metal ions in solution was determined with the use of ICP-OES technique, whereas concentration of metal ions adsorbed on the carbonaceous adsorbent surface was determined by EDXRF spectrometry. Following parameters was studied in order to examine adsorption process: (i) effect of sample acidity, (ii) the influence of foreign ions concentration, (iii) adsorption isotherms (simulated using Langmuir and Freundlich isotherm models) and the maximum adsorption capacity, (iv) kinetics study using the pseudo-first and pseudo-second order rate adsorption kinetic model.

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Poster number **14**

Metabolite profiling of atypical antipsychotic drug - clozapine with the use of human liver microsomes and LC-MS method

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Abstract

Clozapine (8-chloro-11-(4-methylpiperazin-1-yl)-5H-dibenzo[be][1,4]diazepine) is the first of second generation antipsychotic drug indicated for the treatment of schizophrenia and other acute psychosis. It exhibits the properties of the antagonist of serotoninergic and adrenergic receptors and it demonstrates greater efficacy compared to the first generation antipsychotics. Performed study proved that the metabolism of this drug occurs in the liver with the participation of P450 cytochrome isoenzymes.

In this study human liver microsomes (HLM) with NADPH as a cofactor was used for simulation of phase I metabolism reactions. This in vitro method is easy, cheap and fast, which is the reason of its frequent use for mimicking of drugs metabolism.

RP-UHPLC methods coupled with accurate quadrupole-time-of-flight (Q-TOF) mass spectrometry was used to the metabolite profiling of clozapine after the incubation with HLMs. The separation was performed on Kinetex C18 (dp=1.7 µm) UHPLC column and gradient elution with a mixture of acetonitrile and 0.1% solution of formic acid in water was used. Mass spectrometry was performed in auto MS/MS mode in order to collect MS as well as all the fragmentation spectra of parent compound and its metabolites. After two hours of in vitro incubation of clozapine with HLMs seven metabolites were found and structurally characterized. The main metabolites were found as a products of N-oxidation, dealkylation and hydroxylation reactions. UHPLC coupled with Q-TOF high resolution MS method was found to be a powerful tool for the metabolite profiling of clozapine after in vitro incubation with human liver microsomes.

Poster number **15**

Evaluating the advantage of higher heat conductivity of core-shell diamond stationary phase particle in gradient mode chromatography at very high pressure

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Abstract

In a response to requirements for more efficient chromatographic columns new generations of sub-2 µm particles for ultra-high-pressure liquid chromatography (UHPLC) have been developed. Decreasing the particle diameter results not only in lower mass transfer resistances, but also broadens the optimal range of mobile phase flow rates and raises back pressure. However, there are some negative consequences of applying high pressures and mobile flow rates in UHPLC. Viscous friction of the percolating liquid generates significant amount of heat inside the column. The heat generation rate increases rapidly with decreasing particle size and as a result axial and a radial temperature gradients can form inside a column. Temperature gradients, especially in the radial directions, results in broadening of the chromatographic peaks and losses of column efficiency. One of methods to eliminate or at least reduce the temperature gradients is application of material with very high heat conductivity as a stationary phase.

FLARE WP column (Diamond Analytics, USA) with stationary phase based on diamond material of very high heat conductivity compared to conventional silica has been employed in our studies. The particles consists of non-porous carbon cores and porous shells made of diamond nanocrystals. The main attention of study has been focused on measurements of column efficiency in different thermal conditions: (1) natural heat convection in air oven and (2) forced heat convection in water jacket. Insulin was used as a solute with mobile phase flow rates in the range between 0.05 mL/min to 1.1 mL/min in gradient mode. Despite the inlet maximum pressure has reached almost 1000 bar no significant efficiency drop was observed both in the case of forced and natural heat convection conditions. Such a result also confirms that columns with stationary phases of high heat conductivity are efficient in reduction of temperature gradient effects on solute retention.

Acknowledgments

Support for this work was provided by the grant 2015/18/M/ST8/00349 from the National Science Centre, Poland.

Poster number **16**

Correlative analysis of anseriformes feathers

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Abstract

The reveal of diversity in chemical composition of waxes layer as well as structure and properties of feathers between of anseriformes was the aim of the study. The correlative analysis of the feather's, which belonged to anatidae family of gooses such as: Bar-headed, Swan, Emperor, Barnacle and Canadian, opens a way to compose an innovative materials of broad utilitarian application.

The investigation focused on the utilize a thin layer chromatography (TLC), a gas chromatography (GC), an infrared spectroscopy (FTIR), an energy dispersive X-ray spectroscopy performed in the scanning electron microscopy (EDX-SEM) and a scanning electron microscopy (SEM) into disclosing of chemical difference of waxes as well as microstructure details.

The TLC of waxes, collected by extraction in hexane and then chloroform-methanol (2:1 v:v), which were performed on aluminium plates in heksane-diethyl ether-acetic acid medium indicate that Canadian gooses feathers contains highest amount of wax of widest variety of fatty acids. Such result was confirmed by comparison of mass in extraction process as well as GC and FTIR analysis.

The GC investigation suggest that the waxes composition differs between specimens in amount of low and high boiling chemical species. The chloroforme-methanol extracts of Swan goose waxes contains highest amount of high boiling compounds. The highest amount of low boiling components in the same solution occurs in the waxes from Emperor gooses while lowest amount of such groups was detected for waxes of Canadian gooses.

The hexane extracts of waxes from gooses were compared with the standard hexane mixture. The results indicate on Emperor goose wax as such of most wealth in the fatty acids of high molar mass. Whereas Canadian goose wax is combined with lowest amount of such group of acids but highest of low boiling fatty acids.

The FTIR reveal that the feathers difference in quantitative way and EDX-SEM shows that the feathers difference in qualitative way between specimens.

The SEM micrographs analysis facilitated to compare sizes of particular elements of feathers between populations.

Poster number **17**

Thin-layer chromatographic investigation of decomposition of anthocyanes

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Abstract

Anthocyanes are plant pigments largely widespread in the nature. They occur mostly in fruits and flower petals, but also in leaves, shoots and roots. In the nature, anthocyanes can occur as glycosides, which are connected with various sugar moieties, but also as aglycones [1]. It is known that anthocyane compounds can easily decompose by oxidation, hydrolysis and other defragmentation caused by splitting of the covalent bonds. Factors affecting these various kinds of disintegration are high temperature, pH changes, light and exposition to oxygen [2].

Anthocyane standards used in this study were cyanin, which consists of a cyanidin molecule and two molecules of glucose, and keracyanin, which includes cyanidin and one sugar molecule, rutinose. During the tests, gradual change in color of the anthocyanine solutions was noticed, which supported a hypothesis about possible disintegration of these compounds. Due to the presence of sugar moieties in the studied anthocyanines, suspicion of their possible hydrolytic splitting appeared.

The experiments were performed by thin-layer chromatography (TLC) with triple chromatographic development. The Maillard reaction with p-aminobenzoic acid reagent (PABA) was used to confirm the presence of splitted sugars [3]. The results of the TLC analysis were densitometrically evaluated with use of the CD-60 model Desaga scanning densitometer. The obtained results confirm that in the case of, the investigated anthocyanine pigments, these glycosides tend to disintegrate in the employed chromatographic system by total or partial hydrolysis.

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Poster number **18**

Adsorptive properties of cellulose fibers coated with chemically modified amorphous silica

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Abstract

Silica gel is one of the most popular adsorbent applied in analytical chemistry. Silanol groups present on the surface of silica allow covalent attachment of various organosilanes functionalized with various groups, mercapto or amino. Chemical modification of silica results in materials characterized by high chemical and mechanical stability. Silica adsorbents are applied, inter alia, in high performance liquid chromatography (HPLC) as stationary phases, or in solid phase extraction (SPE) for preconcentration or separation of analytes prior to their determination by chromatography or spectroscopy techniques.

The aim of the research was the synthesis and use of modified cellulose membranes as solid sorbents in SPE for the ions preconcentration and their determination by energy-dispersive X-ray fluorescence spectrometry. Membranes were prepared by the synthesis of amorphous silica coatings on cellulose fibers followed by their modification with (3-mercaptopropyl)-trimethoxysilane. The structure of the obtained membranes was characterized by microscopic and spectroscopic techniques. The adsorptive properties of the membranes were verified by study of the following parameters: pH, contact time and sample volume, foreign ions presence, ionic strength and sorption capacity. The membranes were applied in separation and preconcentration of arsenic species.

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Poster number **19**

Fatal poisoning of MDMB-CHMICA, 4-CEC and 4-MEAP

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Abstract

The issue of sudden deaths due to acute MDMB-CHMICA, 4-CEC and 4-MEAP poisoning is presented in the report. The analysis included case autopsied. A 20-year-old man was found dead. Biological material were delivered to the Toxicological Laboratory ToxLab placed in Katowice, during the autopsy were subjected to chemical-toxicological analysis. Samples analyzed by performance liquid chromatography coupled with mass spectrometer and PDA detector (LC-PDA-MS). Analysis of blood samples present concentration of the MDMB-CHMICA were 5,1 ng/ml, 4-MEAP were 60 ng/ml and 4-CEC were 70 ng/ml.

Poster number **20**

Chemometric study of the HPLC-DAD-FLD-MS analysis of Tamoxifen photodegradation process

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Abstract

The study of the photodegradation effects induced by UV-light on tamoxifen (TAM) in water has been performed. The stability profile of this drug has recently received considerable interest due to its increasing occurrence in environmental sample matrices (TAM is frequently used to treat some types of breast cancer in men and women) [1]. An advanced and powerful chemometric approach is proposed for the analysis of the multiset data obtained in the simultaneous chromatographic analysis performed using UV-DAD, FLD and MS detection.

In this work, a TAM solution was irradiated in a light cabinet SUNTEST according to Q1B ICH guideline. The obtained degradation profiles were monitored by UV spectrophotometry as well as with a fluorescence detector. Some aliquots at different reaction times were further analyzed by HPLC-DAD-FLD-MS. The Multivariate Curve Resolution-Alternative Least Squares (MCR-ALS) chemometric method was applied to describe the drug photodegradation process. This strategy involved the simultaneous analysis of multiple experimental data sets from different analytical platforms [2], including UV spectrophotometry, fluorescence spectroscopy and DAD/FLD/MS-chromatography [3]. The simultaneous description of the kinetic photodegradation process of this drug and the MS identification of the products formed after light exposure, together with the new information obtained from their pure excitation and emission UV spectra, will allow the full description of the studied system, and contribute to the understanding and evaluation of the environmental risk assessment and fate of these photoproducts.

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Poster number **21**

Trehalose, mannitol and arabitol as indicators of fungal metabolism in geological sedimentary rocks

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Abstract

Trehalose, mannitol and arabitol are the main sugars of extant fungal metabolism, but their occurrence and distribution in geological sedimentary rocks have rarely been considered. Here, we identify these mono- and disaccharides in Miocene lignites [1] and for the first time in Late Cretaceous mudstones and coals. The co-occurrence of trehalose, mannitol and arabitol in the geological materials suggests their fungal origin, because these three saccharides are major compounds present in most modern fungi, including the very common in nature mycorrhizal and wood-rotting groups. Therefore, we conclude that these sugars should be treated as new fungal biomarkers (biomolecules) present in geological rocks. Trehalose and mannitol are major compounds in total extracts of the samples and a sum of their concentration reaches 4.6 μg/g of sample. The arabitol concentrations do not exceed 0.5 μg/g, but in contrast to trehalose, the concentration correlates well with mannitol, suggesting that they have the same, translocatory role in fungi. Based on the trehalose vs. mannitol and arabitol distributions in Cretaceous samples and their comparison with data for modern fungi, we preliminarily conclude that the coal seams from the Rakowice Małe section were formed during diverse climatic periods than the overlying sediments. Furthermore, no DNA could be isolated from the samples of lignites and overlying sediments, whereas it was abundant in the control samples of maple, birch and oak wood degraded by fungi.

Other saccharols and sugar acids like D-pinitol, quinic acid and shikimic acid, were found for the first time in sedimentary rocks, and their source is inferred to be from higher plants, most likely conifers. The preservation of mono- and disaccharides of fungal origins in pre-Palaeogene strata implies that compounds previously thought as unstable can survive for tens to hundreds of millions of years without structural changes in immature rocks unaffected by secondary processes.

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Poster number **22**

Bacterially derived hopanes with biological configuration from Ediacaran sedimentary rocks of the East European Craton

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Abstract

Thermodynamically unstable hopanes with a characteristic biological $\beta\beta$ configuration, together with hopenes, hopanoic acids and hopanols were identified as important constituents of Ediacaran to Cambrian (560 – 530 Ma) sedimentary rocks of the East European Craton. Relatively high concentrations of $\beta\beta$ hopanes in relation to $\alpha\beta$ hopanes were identified in the Petersburg area and eastern Belarus, while in Volyn samples these compounds were found in traces. In addition, polar hopanoids including hopanols and hopanoic acids were found in most of the Petersburg and some Belarus and Volyn sedimentary rocks. The estimated equivalent of vitrinite reflectance for samples of lower maturity, measured based on $C_{31}\beta\beta$/(S + R + $\beta\beta$) ratio is in the range 0.28–0.49% Rr, while for those of higher thermal maturity this parameter corresponds to 0.41–0.57% Rr. The values of the C_{31} 22S/(S + R) ratio are in agreement with above data and are in the range of 0.1–0.3 for the Belarus and Petersburg samples, of 0.3–0.4 for Volyn, and of 0.4–0.5 for Lithuania, where $\beta\beta$ hopanes and hopanols were not detected or are present as traces. Moreover, there is good correlation (R^2 = 0.8) between $C_{31}\beta\beta$/(S + R + $\beta\beta$) and C_{31}ENE/(H + ENE) ratio values (defined as ratio of C_{31} hopenes to $\alpha\beta$ hopanes), which proves that less-stable $\beta\beta$ hopanes and hopenes are enriched in the same immature sedimentary rocks. The remarkable occurrence of hopanes with biological configuration in the very old Ediacaran to Cambrian rocks confirms the assumption that geological time plays an insignificant role in the diagenetic transformation of organic matter.

Acknowledgments

Authors acknowledge financial support from the Polish National Science Centre MAESTRO grant 2013/10/A/ST10/00050.

Poster number **23**

A comparison of several supervised methods for modelling time-course chromatographic data

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Abstract

One of the ongoing challenges in metabolomics is related to multivariate analysis of the so-called time-course data. The reason to conduct a time-course experiment is to understand biochemical response mechanism in organisms by investigating changes of metabolic profiles over time. Often chromatographic methods are adopted for analysis, since the samples are complex mixtures and one is interested in tracing the content/concentration changes of as many metabolites as possible. A possible option is to use the resulting chromatograms as unique sample fingerprints or to determine the contents/concentrations of some selected metabolites. Either way the collected multivariate experimental data require a further chemometric analysis in agreement with the aim of the study.

A chemometric strategy for analysis of time-course data is to find common content/concentration profiles that describe the changes over time with the use of principal component analysis, PCA [1] and multivariate curve resolution, MCR [2]. However, the results obtained from these methods may not be optimal when the between-subject variability has a predominant influence. In order to account for different sources of variation associated with the time and subject effects, multivariate supervised methods that combine analysis of variance, ANOVA, for each metabolite and principal component analysis, PCA, simultaneous component analysis, SCA, or target projection, TP [3, 4] for collected effect matrices are used. The appropriate variant of ANOVA for the time-course data analysis is repeated measures analysis of variance [5].

The goal of this study was to implement repeated measures analysis of variance in three supervised methods ANOVA-PCA, ASCA and ANOVA-TP [4] and to compare the performances of these for modelling of time-course chromatographic data. Variables that contributed most to observed differences in chromatograms with respect to a given effect were also identified.

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Poster number **24**

Identification of the ZIKA virus protease NS3 targets with *nano*LC-MALDI-TOF/TOF.

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Abstract

Zika is a human flavivirus transmitted by *Aeders mosquito*. Zika virus cause severe damage in the brain development stage of newborn babies what results in serious neuronal disfunctions in adults. A global research to identify effective treatment options showed that the viral NS2B-NS3 protease represents an attractive target due to its crucial role in the viral infection cycle. Activity of viral protease NS3, is crucial during the early stage of infection, but in fact there is no unambiguous answer what is the target of the protease action. Application of quantitative proteomics can be helpful in finding the changes that occur at the cell during Zika infection.

In the present study, NS3 protease (cloned in the *E. coli* model) was introduced into the 293T cells. Simultanously, introduction of the mutant, inactive form of this protease ($S^{195} \rightarrow A$) was a control. To find the expression changes in the proteome between NS3 protease treated cells and the control ones, iTRAQ labeling was combined with of off-line nano liquid chromatography-matrix assisted laser desorption/ionization tandem mass spectrometry (*nano*LC-MALDI-TOF/TOF).

Design and optimization of the robust proteomic approach to study action of the NS3 protease, allowed for providing the results of great interest and importance in viral infection investigations. Such achievements may be useful for further research in this field.

Poster number **25**

A simplified method for the determination of lipoic acid and other thiol amino acids in human plasma

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Abstract

Thiols are low molecular chemical compounds containing sulfhydryl groups in their structures. From a metabolic point of view, the most significant thiols present in the human body are: homocysteine (Hcy), cysteine (Cys), cysteinylglycine (Cys-Gly) and glutathione (GSH). These compounds perform important functions in cell biology and biochemistry and also play an essential role in various physiological and pathological processes of human body [1].

α-Lipoic acid (LA), also known as 6,8-dithioctanoic acid, is an eight-carbon saturated acid, containing two sulphur atoms [2]. LA is a natural ubiquitous compound which is distributed in cells of all eukaryotic and prokaryotic organisms, microorganisms, plants, animals and humans [3]. It is also an unique antioxidant of many biological systems. Humans can synthesize LA "de novo" from fatty acids and Cys, but only in very small amounts. For the reason, LA needs to be absorbed from exogenous sources, mainly from dietary supplements [2].

The aim of this work was to develop a sensitive and simple analytical method allowing the simultaneous determination of selected metabolically important sulphur compounds, such as Cys, Hcy, GSH, Cys-Gly and LA in plasma samples. The tests were carried out by reversed phase high performance liquid chromatography with UV-VIS DAD detection. The crucial innovation of sample preparation procedure in the presented method was based on an omission of the plasma protein deprotenization step. The selection of optimal conditions for sample preparation for the analysis was carried out using plasma samples injected with analytes of interest. Due to the necessity of reduction and derivatization of plasma components the amount of the reducer, tris-2-carboxyethyl phosphine, time of reduction, quantity of the derivatizing reagent, 1-benzyl-2-bromopyridinium bromide, and the time of derivatization reaction were studied.

The developed method is characterized by the linearity of the detector's response in the tested concentration ranges for each of the analytes with the correlation coefficient of $R>0.999$ in each case.
The limit of detection and quantitation were determined as well. For Cys, Hcy, GSH, Cys-Gly LOD was 0.12 nmol/mL, for LA was 0.08 nmol/mL. LOQ for Cys, Hcy, GSH, Cys-Gly was 0.2 nmol/mL and for LA was 0.12 nmol/mL.

The developed method was successfully applied for the analysis of plasma samples of volunteers after LA supplementation.

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Acknowledgement

This work was supported by grants from the National Science Center (2013/09/D/ST5/03909) and University of Lodz.

Poster number **26**

Chromatographic and chemometric methods for tracing illegal removal of fiscal markers from diesel oil fuel

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Abstract

Since 2003 the European Union law requires indication of low tax level diesel oil by spiking it with an invisible marker compound Solvent Yellow 124 [1]. In many countries visible indicators (dyes changing color of fuel) are used. In Poland two red dyes either Solvent Red 19 or 164 are considered interchangeably [2]. Even though the selected substances are deemed to be stable, there are many illegal attempts to modify their physico-chemical properties, and thus to eliminate their role as specific fiscal markers (e.g. using acidic hydrolysis, adsorption and/or reduction agents).

Our previous study [3,4] was focused on evaluating physico-chemical changes observed in low tax diesel oil samples treated with an adsorption agent. The major goal of the present study is to gain knowledge of changes in diesel oil samples induced by a reducing agent.

To describe the studied phenomenon, 29 genuine diesel oil samples, spiked simultaneously with Solvent Yellow 124 and Solvent Red 19, were selected. Simulation of sample treatment, involving reducing agent, was carried out in a laboratory. Samples before and after the treatment were characterized by their chromatograms obtained from gas chromatography with mass spectrometry detection.

In order to identify the differences in chemical composition of diesel oil samples the partial least squares discriminant analysis extended with variable selection method was used. Identification of relevant variables was carried out with three variable selection methods: the selectivity ratio, uninformative variable elimination and the variable importance in projection method. The discriminant models were validated using the Monte-Carlo framework [4]. Obtained results provide evidence of chemical differences observed in diesel oil samples before and after their treatment.

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Acknowledgement

MD, JO acknowledge the support of the National Science Centre, Poland (research grant no. 2014/13/B/ST4/05007).

Poster number **27**

Chromatography in peptide synthesis

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Abstract

Since 1963, when Robert Bruce Merrifield developed the method of synthesizing tetrapeptides on the polymer support, solid-phase synthesis has significant impact on chemistry of peptides. In this method, the C-terminal amino acid is attached to an insoluble support, and then next amino acids are added to the first residue, without need of crystallization of intermediate products. Thus, washing and coupling procedures become much easier. One of the most important part of peptide synthesis is purification of the product. In some cases by-products, generated during synthesis, are structurally similar to the main sequence, which demands the use of high resolution method of separation. As a standard in purification of peptides High Performance Liquid Chromatography (HPLC) is used.

Our research is focused on synthesis, identification and purification of arginine-containing peptide as convenient substrate for detection of peptidases. The guanidine group of arginine was protected with Pbf group, which is the most commonly used protecting strategy for this amino acid. However, in some cases, the removal of such group during global deprotection is problematic, which can be a source of undesired products. To obtain our peptide, Fmoc solid-phase synthesis with application of carboxyl group activating reagent, such as COMU has been used. To confirm structure of the obtained compound, MALDI-TOF/TOF mass spectrometry has been used. To purify the obtained peptide, HPLC with reversed phase column has been applied.

In this research, description of synthesis of arginine-containing peptide, mass spectrum and chromatogram of this peptide are presented. The obtained results show, that the use of HPLC led to the separation of the main product, in which removal of Pbf was complete, from the by-product with incompletely deprotected side chain of arginine residue.

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Poster number **28**

Application of single drop microextraction for the determination of homocysteine thiolactone by capillary zone electrophoresis

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Abstract

Homocysteine thiolactone (HTL) as an intramolecular thioester plays an important role in human health, because by forming isopeptide bonds with amino groups of the lysine protein it impairs or changes its biological function. HTL is generated from homocysteine, due to an error-editing reaction during protein biosynthesis, when this amino acid is mistakenly selected instead of methionine by methionyl-tRNA synthetase. The presence of HTL in the human organism, especially at increased concentrations, may be related to the development and progression of cardiovascular diseases [1].

The content of HTL in the human organism is very low and, depending on the type of analyzed biological sample, its maximal concentration may be about 0.5 μmol/L (for human urine) [1, 2]. Therefore, it is important to develop effective analytical methods which allow to study concentration of this compound at levels as low as possible. Some of developed methods use the capillary electrophoresis technique (CE). However, due to the miniaturized separation system, i.e. the capillary in combination with a commonly used UV-Vis detector, it is very difficult to effectively monitor the content of HTL in human organism. For this purpose, more sensitive detectors are used, e.g. mass spectrometer, sample stacking methods in CE measurement system or microextraction techniques. One of these techniques is single drop microextraction (SDME), which can be easily performed in CE system in on-line mode. The advantage of SDME is the easiness of automating the extraction process. Another extremely important feature in HTL determination is that the SDME is characterized by a high enrichment factor. In addition, it allows for sample cleanup and significantly reduces the consumption of toxic organic solvents [3].

The aim of the work was to develop a new analytical procedure for the determination of HTL using SDME coupled with the CE system. The separation in the method was carried out in a bare fused-silica capillary (75 μm i.d., effective length of 55.5 cm), the background electrolyte used was 0.1 mol/L, pH 4.75 phosphate buffer, separation voltage of 24 kV was applied and UV detection at analytical wavelength 240 nm. The method was validated under optimized experimental conditions. Five-point calibration plot was made for HTL in triplicate according to optimized procedure. The calibration curve for HTL was linear in the tested range 0.1-10 μmol/L. The equation for the linear regression line was $y = 8.5575x - 0.0814$ with $R2 = 0.9999$. The precision of the method expressed as relative standard deviation value did not exceed 9.2% and recovery values ranged from 91% to 103%. Experimentally determined limit of quantification for HTL was 0.1 μmol/L.

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Acknowledgements

This work was supported by University of Lodz.

Poster number **29**

PAHs analysis as a method for detection of domestic wastes combustion in central heating furnaces

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Abstract

Polycyclic aromatic hydrocarbons are a complex group of organic compounds containing two or more condensed aromatic rings. They are formed in high-temperature pyrolysis of fossil fuels and thus they became indicators of incomplete combustion process. Moreover their negative influence on human health have attracted additional attention. In present study we have investigated correlation between combustion of domestic wastes and PAH content in furnace ash. Examined samples were obtained by combustion of known mixtures of plastic wastes and coal. Two analytical methods have been utilized. First based on extraction with organic solvents and subsequent analysis by gas chromatography (GC-MS). Second based on pyrolytic gas chromatography (Pyro-GC-TOFMS). In both cases mass spectrometers were utilized as detectors. Special attention was paid on sixteen polycyclic aromatic hydrocarbons : naphthene, acenaphthene, acenaphthylene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, chrysene, benzo(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, benzo(b+k)fluoranthene, dibenzo(a, h)anthracene+ indeno(1,2,3-cd)pyrene, benzo(g, h, i)perylene, perylene.

Poster number **30**

Application of Salting-Out Thin Layer Chromatography to the Separation of Selected Amino-Acids

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Abstract

Amino acids are essential ingredients of diets of all living beings and biologically important biochemical molecules commonly used in nutritional supplements. Because of the prevalence of amino acids in many biological systems chromatographic study of these molecules is very important. Thin layer chromatographic techniques have been used to detect and quantify aminoacids for many years. Aminoacids are separated most frequently by NP TLC on silica gel or cellulose and RP TLC (usually on RP-18 plates), but other supports (alumina, talc, starch, NH2, CN or diol-modified silica), impregnated adsorbents (silicagel impregnated with metal ions, or surfactants) are also used. Mobile phases used for the aminoacids separation are sometimes modified with surfactants, metal salts or cyclodextrines; micellar or microemulsion mobile phases are also used.

The objective of this study was to investigate the possibility of using salting-out thin layer chromatography (SOTLC) [1] to separate the selected aminoacids (glycine, serine, proline, methionine, hydroxyproline, tyrosine, cysteine, arginine, β-phenylalanine, leucine, aspartic acid, isoleucine, α-alanine, tryptophan, β-alanine. The chromatographic separation was attempted on silicagel 60 and cellulose, using aqueous solutions of the following salts: KBr (4 mol/L, 2 mol/L), NaCl (4 mol/L, 2 mol/L), NH4Br (2 mol/L), (NH4)2SO4 (4 mol/L, 2 mol/L), Mg(NO3)2 (1.5 mol/L), MgSO4 (2 mol/L), ZnSO4 (1.5 mol/L), CaCl2 (4 mol/L), KCl (4 mol/L), KNO3 (2 mol/L), NH4Cl (4 mol/L), NH4Br (4 mol/l) as mobile phases. It was established that cellulose is, generally speaking, not a suitable adsorbent for SOTLC separation of studied aminoacids - the only (moderately) successful separation achieved by SOTLC on cellulose was with ammonium sulfate (4 mol/L); in the case of the other salts almost all aminoacids migrated with the solvent head or the spots were distorted. The separation was considerably better on silicagel 60, especially with KBr (2 mol/L), KCl (mol/L), NaCl (4 mol/L) and (NH4)2SO4 (4 mol/L).

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This research was supported by an internal grant of the Medical University of Łódź no. 503/3-016-03/503-31-001

Poster number **31**

Validation of HPLC-DAD method for schisandra lignans estimation and application of the method for Schisandra chinensis cv. Sadova fruit and leaf extracts analysis

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Abstract

Schisandra chinensis (Turcz.) Baill. – is a native to China, pharmacopoeial species of documented therapeutic importance. The raw material is the schisandra fruit with e.g. hepatoprotective, adaptogenic, antitumour, immunostimulant, anti-ulcer, antioxidant and detoxifying, antiviral and antimicrobial activities [1]. The main group of secondary metabolites which are unique to this species and responsible for its biological activities, are dibenzocyclooctadiene lignans, also called 'schisandra lignans' (SL).

In the present study, Ukrainian cultivar of S. chinensis - cv. Sadova, was investigated for SL production. The validation of the SL determination method was successfully elaborated under the study.

HPLC-DAD method was applied for phytochemical qualitative and quantitative analyses of fruit and leaf methanolic extracts of plants growing in Poland. Under the study nine standards: gomisin A and G, deoxyschisandrin, schisandrin, schisandrin C, γ-schisandrin, schisantherin A and B and schisanthenol were used.

Analysis of SL was performed acc. to Zhang et al. [2]. Separation was performed using a Kinetex C-18 analytical column on Hitachi LaChrom Elite HPLC system with gradient program. Detection wavelength was set at 225 nm. Validation of the method was performed by determination of typical parameters: accuracy, precision, linearity, limit of detection (LOD) and limit of quantification (LOQ) [3].

The results indicated that the proposed method was characterized by high sensitivity; LOD for SL was placed between 0.0044 - 0.0372 mg/ml. Percentage recovery of SL presented as mean values for three concentration levels was high and ranges from 95.77% to 103.90%. Satisfactory precision determined for three concentration levels was confirmed by the values of variability coefficients relative standard deviation which are in the range from 0.21% to 2.96%. Linearity of the tested substances was preserved in a wide range (from 0.0013 mg/ml to 1.0000 mg/ml).

The concentrations of the individual SL in the studied extracts varied within a broad range, from 2.6 to 166.8 and from 1.40 to 55.13 mg/100 g DW, in fruits and leaves, respectively. The total SL content in fruit and leaf extracts was equal 646.0 and 240.8 mg/100 g DW, respectively.

The applied method was effective for SL estimation. Results documented that fruits of S. chinensis cv. Sadova could be valuable raw material for pharmacy purposes.

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Acknowledgements: This study was funded by National Science Centre, Poland: grant number 2016/23/D/NZ7/01316.

Poster number **32**

Application of the HPLC technique for the assessment of the hydrolytic stability of carbamazepine and its transformation products

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Abstract

Pharmaceuticals are considered as "emerging pollutants", which have raised attention since first references regarding their presence in the wastewaters and surface water became available [1]. One of the most popular medicine is carbamazepine (CBZ) - anticonvulsant and mood stabilizer. Total consumption of this drug in 2013 in EU was 351 tons [2]. CBZ is frequently found in surface water and wastewater treatment plants effluents [3,4]. Such high demand and constant load delivered to the environment result in the need to increase the knowledge of the persistency of carbamazepine in water bodies. Moreover, CBZ, like every other pharmaceutical, is transformed in an organism and environment to derivates, which should be included in general experiments regarding environmental issues. Taking into account everything mentioned above, hydrolytic stability of CBZ and three transformation products: carbamazepine epoxide (ep-CBZ), 2-hydroxy carbamazepine (2-OH-CBZ) and 10-hydroxy carbamazepine (10-OH-CBZ) was investigated. The experiments were conducted according to OECD Guidelines for the testing of chemicals number 111: Hydrolysis as a function of pH. The preliminary experiments conducted in pH 4, 7 and 9 in the temperature of 50 °C for 5 days showed that only carbamazepine epoxide in pH 4 degraded completely. Other analytes remained intact and may be considered hydrolytically stable for at least a year in the temperature of 25 °C [5]. Extended experiments for ep-CBZ were performed due to its instability, which allowed to calculate basic parameters of the hydrolysis process, such as rate constant, half-life of the compound and activation energy. For all of the experiments HPLC-UV-Vis technique was applied to determine the levels of compounds in the samples. The assessment of the stability of analytes was performed by comparing the area of the peak representing the compound which did not underwent any experiments (control sample) with the one that was incubated. For each compound simple analytical method was developed and validated.

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Financial support was provided by the National Science Centre under grant OPUS 2015/17/B/NZ8/02481

Poster number **33**

Method development for determination of steroidal glycoalkaloids in food using gas chromatography

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Abstract

The Solanaceae family includes a number of economically important cultivated species, such as tomato (*Solanum lycopersicum*), potato (*S. tuberosum*) and eggplant (*S. melongena*). They all contribute many beneficial phytochemicals to the human diet (e.g. antioxidants, minerals and vitamins), as well as non-nutritive compounds as glycoalkaloids (GAs) – heterocyclic compounds composed of carbohydrate side chain attached to 3-OH group of the skeleton of cholestane (aglycone), via glycosidic bond. Steroidal glycoalkaloids are defensive factors against threats posed by pests and phytopathogens, characterized by broad-spectrum of activity (from microorganisms to vertebrates). They display certain antifungal, antibacterial and anticarcinogenic properties [1]. The consumption of high-glycoalkaloid diet (more than widely accepted "safety limit" of 200 mg/kg FW of total GAs) was reported to cause severe illnesses affecting digestive system (vomiting, diarrhea) and nervous system (disorientation, vision problems), or even death. Therefore, it is important to determine their content in food.

The aim of the study was to develop the analytical method for determination of steroidal glycoalkaloids in food using gas chromatography. The evaluation of three acid anhydrides for blocking the polar nitrogen atom in spirosolane type aglycones (to which tomatidine and solasodine belongs) was carried out first. The procedure included acid hydrolysis of model substance (tomatine), and two-stage derivatization of liberated aglycone: silylation with MSTFA and acylation of nitrogen atom using three halogenated acid anhydrides: pentafluoropropionic acid anhydride (PFAA), trifluoroacetic acid anhydride (TFAA) and chlorodifluoroacetic acid anhydride (CDFAA). The reaction was carried out in different time and temperature combinations. The parameters used as criteria for the selection of optimal conditions included relative response (to the I.S.) and repeatability of the method. The identification of obtained derivatives was carried out using gas chromatography-mass spectrometry (GC-MS) and the quantitative analysis was performed using gas chromatography with flame ionization detector (GC-FID). Then, using the anhydride chosen (TFAA), the method was validated and applied for determination of glycoalkaloids in commercially available food, which include several types of fruits and tubers of cultivated potato, tomato and eggplant obtained from the local market. Compounds were extracted from homogenized plant material using aqueous acetic acid solution, purified using liquid-liquid extraction, and subjected to hydrolysis and derivatization as described above. The results suggest high usefulness of the method in routine glycoalkaloid determination in food samples of plant origin.

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Financial support was provided by University of Gdansk under grants No. 538-8610-B803-17

Poster number **34**

Application of the simple and easy-to-access chromatographic (RP-18 TLC) and calculated *in silico* descriptors to predict the Blood-Brain Barrier permeability of a large and structurally diverse set of compounds

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Abstract

The Blood-Brain Barrier (BBB) permeability of a drug is an important factor governing the drug's ability or inability to act upon the Central Nervous System (CNS). The measures of the BBB permeability used throughout this study are log BB (the blood/brain partitioning coefficient at equilibrium conditions) measured *in vivo* (BB vivo) or calculated according to the equation: B2 = log BB = 0.547 – 0.016 PSA [1].
Useful yet simple models of the BBB permeability were developed by the Stepwise Multiple Regression Analysis and based on the chromatographic parameters Rf and Rf/PSA obtained by RP-18 TLC with acetonitrile - pH 7.4 phosphate buffered saline 70:30 (v/v) as mobile phase. The chromatographic parameters were combined with some easily calculated molecular descriptors - the number of H-bond donors (HD), the number of H-bond acceptors (HA), energy of the highest occupied molecular orbital – (eH), energy of the lowest unoccupied molecular orbital (eL), to furnish the equations:

B2 = 0.93(±0.27) – 0.15(±0.01) HA – 0.19(±0.27) HD + 0.06(±0.02) eH + 0.02(±0.00)eL + 0.16(±0.10)R_f + 1.78(±1.09) Rf/PSA
R= 0.94; R^2= 0.90; F= 196.52; p<0.00000 s = 0.23038; n=154

B2 = 0.46(±0.05) – 0.16(±0.01) HA – 0.19(±0.01) HD + 2.94(±1.09) Rf/PSA
R= 0.93; R^2= 0.90; F= 342.74; p<0.00000 s = 0.24540; n=154

The results of the chromatographic analysis proposed in this study (RP18 TLC) are a source of valuable information on the ability of compounds to cross the BBB. This simple, inexpensive and very rapid method may be used to assess the BBB permeability of compounds isolated or synthetized on a very small scale, sufficient just for a thin layer chromatographic experiments.

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This research was supported by an internal grant of the Medical University of Łódź no. 503/3-016-03/503-31-001.

Synthesis and identification of derivatives of 4,7-dichloro-1,10-phenanhtroline

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Abstract

1,10-Phenanthrolines are bident ligands due to the presence of two lone electron pairs on both adjacent nitrogen atoms. They coordination abilities are results of presence of the lone pairs of electrons on the both nitrogen atoms located in characteristic shape of heterotricyclic system. Until now were develop a lot of applications for them. For instance in photovoltaics 1,10-phenanthrolines are used to improve the contact area of one of the layers in organic cells and its use has reduced production costs [1,2].

Twenty two derivatives of 4,7-dichloro-1,10-phenanthroline, their 4,7-di(pyrrolidin-1-yl), 4,7-di(9H-carbazol-9-yl) and 4,7-di(10H-phenothiazin-10-yl) with sixteen novel structures have been synthesized in an efficient synthesis protocols. The presented protocols allow to obtained titled compounds with the yields up to 96%. Their properties have been characterized by the combination of multinuclear NMR, MS, HRMS, GC-MS and electronic absorption spectroscopy. 5-Fluoro-2,9-dimethyl-4,7-di(pyrrolidin-1-yl)-1,10-phenanthroline has been structurally characterized by X-ray crystallography. Selected 1,10-phenanthrolines were additionally characterized by 13C and 15N NMR spectroscopy in the solid state and compare with commercially available 1,10-phenanthrolin-5-amine.

In this presentation we would like to focus on GC-MS technique. The presented 4,7-dichloro-1,10-phenanthrolines show preferential fragmentation with the initial loss of chlorine, followed by the loss of second chlorine and further decomposition.

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Poster number **36**

Application of stir bar sorptive extraction to the determination of polycyclic aromatic hydrocarbons in aqueous samples

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Abstract

One of the main problems for the analysis of organic pollutants in various matrices, especially in water samples, is the detection of target analytes at the low concentrations.

Sample pretreatment prior to the chromatographic analysis is considered as the most critical step in the overall analytical process since it plays a key role in analyte extraction, pre-concentration and cleanup from co-existing species. Polycyclic aromatic hydrocarbons (PAHs) are important priority organic pollutants due to their harmful and partly carcinogenic, mutagenic and genotoxic properties.

Preferred methods for the determination of PAHs in aquatic samples are solid-phase extraction (SPE), liquid-liquid extraction (LLE) or solid-phase microextraction (SPME) combined with liquid chromatography (LC) or gas chromatography (GC).

In the last decades, the development of miniaturized sample preparation techniques, which reduce or eliminate solvent consumption, has become a dominant trend in Analytical Chemistry. Among these techniques, stir bar sorptive extraction (SBSE) in combination with liquid chromatography has been applied satisfactorily for the analysis of PAHs aqueous samples. In the SBSE technique, the sample is stirred with a glass enclosed magnetic stir bar coated with a layer of polydimethylsiloxane (PDMS) resulting in a distribution of analytes between the aqueous sample matrix and the PDMS layer. Simplicity of operation, rapidity, low sample volume, and high pre-concentration factor are some advantages of this technique.

The aim of this study was to apply SBSE to the determination of PAHs in aqueous samples. Optimum extraction parameters were determined depending on the expected concentration of PAHs in water. Special attention was paid to the desorption process.

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Poster number **37**

The assessment of carbamazepine and 10,11-dihydro-10-hydroxy carbamazepine sorption in soil

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Abstract

Nowadays over 700 emerging pollutants (EPs) are found in the aquatic environment. EPs are synthetic or natural chemical compounds that are not monitored despite being present in the environment. In many cases, the penetration of EPs into the environment has been a long-term phenomenon and was unknown until the development of methods for detecting those impurities. Collected data about their environmental fate and ecotoxicity often are incomplete. EPs can get into the environment by point sources of pollution, for example from wastewater treatment plants and urban/industrial areas, or from nonpoint sources such as atmospheric deposition or food production. One of the main groups of compounds included in EPs are pharmaceuticals. Carbamazepine is a medication used primarily in the treatment of epilepsy and neuropathic pain. Oxcarbazepine is medication used as a substitute for carbamazepine in the treatment of epilepsy. Oxcarbazepine is largely metabolized to pharmacologically active

10,11-dihydro-10-hydroxy carbamazepine. Static sorption tests were carried out for two soils with different physicochemical parameters, in accordance with OECD 106. High-performance liquid chromatography with spectrophotometric detection was used to determine the remaining concentration of pharmaceuticals in the aqueous phase in sorption/desorption equilibrium, from which the concentrations of the carbamazepine and 10,11-dihydro-10-hydroxy carbamazepine isolated in the soil structures were calculated. This enabled the determination of the time of the sorption/desorption equilibrium, the sorption coefficient (Kd) and the impact of changes in environmental parameters on the sorption potential of selected compounds. The collected data allowed the estimation of the mobility of compounds in the soil environment. Sorption coefficient for carbamazepine (2.56 ± 0.05 L kg-1) was higher than for 10,11-dihydro-10-hydroxy carbamazepine (0.37 ± 0.04 L kg-1) which means that its metabolite will show greater mobility in the soil environment.

Acknowledgements

Financial support was provided by the National Science Center under grant 2015/17/B/NZ8/02481

Poster number **38**

Sorption properties of selected HILIC columns on the example of quercetin, phenol and caffeine as test substances

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Abstract

Analytical-scale investigations of the retention mechanism are undoubtedly very helpful in processes of method development, however to obtain more reliable picture of the retention process, the adsorption studies in nonlinear (overloaded) conditions are also required. In these studies adsorption isotherms are particularly important. The determination of adsorption isotherms and the following treatment and interpretation of the isotherm data is of the utmost importance for preparative separation systems understanding. The adsorption isotherm comprises essential thermodynamic parameters required for computer simulations (for e.g. process optimization). Besides, the shape of the isotherm and the adequate isotherm model provides information about the retention mechanism in a tested column.

The aim of this study was to recognize the interactions between selected compounds exhibiting different properties using diol- Acclaim Mixed Mode HILIC-1, zwitterionic Knauer Eurospher II HILIC and Purospher Star NH2 columns. The studies were conducted using various methanol – water and acetonitrile – water systems as mobile phases and quercetin, phenol and caffeine as test substances.

The investigations were conducted according to the following approach. First, basing on the determined raw adsorption data classical Scatchard plots were used to make preliminary selection of the adsorption isotherm type. Next, the degree of heterogeneity of the stationary phase was determined by calculation of the adsorption energy distribution (AED) and finally proper adsorption isotherm models were proposed by fitting to the experimental adsorption data assisted by statistical evaluation.

Poster number **39**

Effect of thermal conditions on the retention behavior of selected test substances in a diamond-based core-shell Flare HILIC column

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Abstract

Diamond columns are based on porous nano-diamond core shell support. The diamond core-shell particles are composed of solid spherical carbon core which is covered by functionalized porous diamond nanocrystals. This composite can tolerate high temperatures, wide range of pH and also features much higher thermal conductivity comparing to silica. That means the potential application areas are very promising involving pharmaceutical industry and biomedicine.

The aim of the work was experimental and theoretical comparison of the applied temperature effect on selected analytes retention using FLARE HILIC diamond column (100 mm x 2.1mm, 3.6 µm particle size, 120Å pore size by Diamond Analytics, USA). The experiments were conducted employing two different thermal conditions: (1) natural heat convection in air thermostat and ^{2} forced heat convection in water jacket, both within temperature range from 293 to 323 K. Water-methanol and water-acetonitrile systems were used as mobile phases with organic solvent concentration ranged from 60% V/V to 90% V/V and phenol and caffeine were used as test analytes.

The obtained results confirm significant impact of temperature and as well as of the applied thermal conditions on the retention process. The global sorption processes of all tested compounds were exothermic as recognized by van't Hoff equation parameters' regression. According to the obtained data retention of the tested substances is more evident in the case of a column working in natural convection oven conditions. Possible mechanisms responsible for the retention have been proposed on the basis of the gathered experimental data.